High Specific Energy Batteries for Future Missions to Icy Worlds

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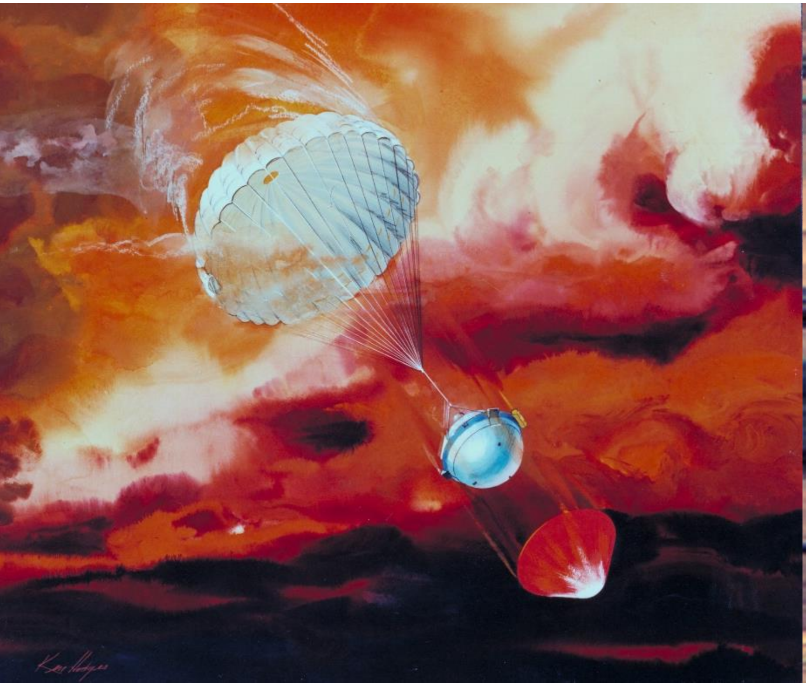
Outline

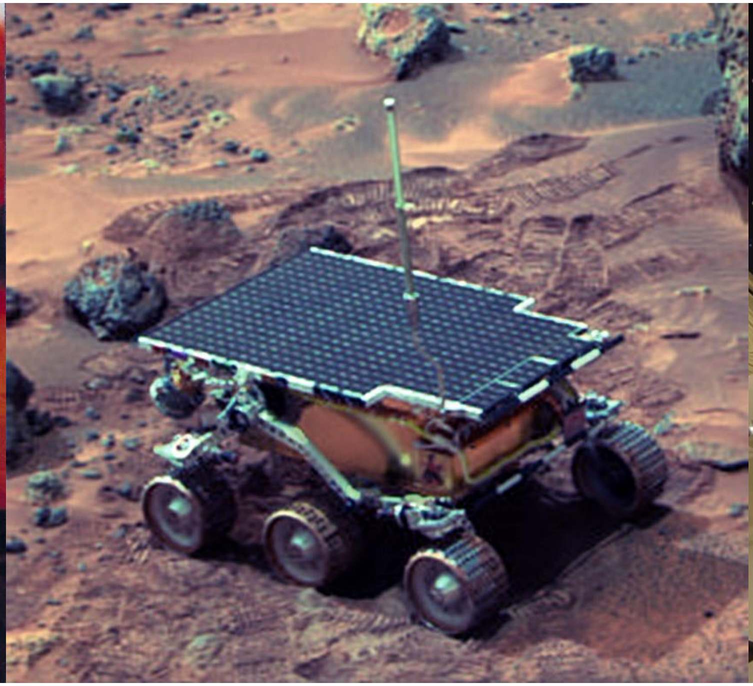
- Lithium primary battery performance testing
  - Rate testing
  - Temperature testing
  - Radiation testing
  - Storage testing
- Experimental lithium primary cell testing
  - Dry heat microbial reduction
- Experimental lithium-ion cell testing
  - Plating during charging at low temperature

Three Examples of Primary Batteries for Space

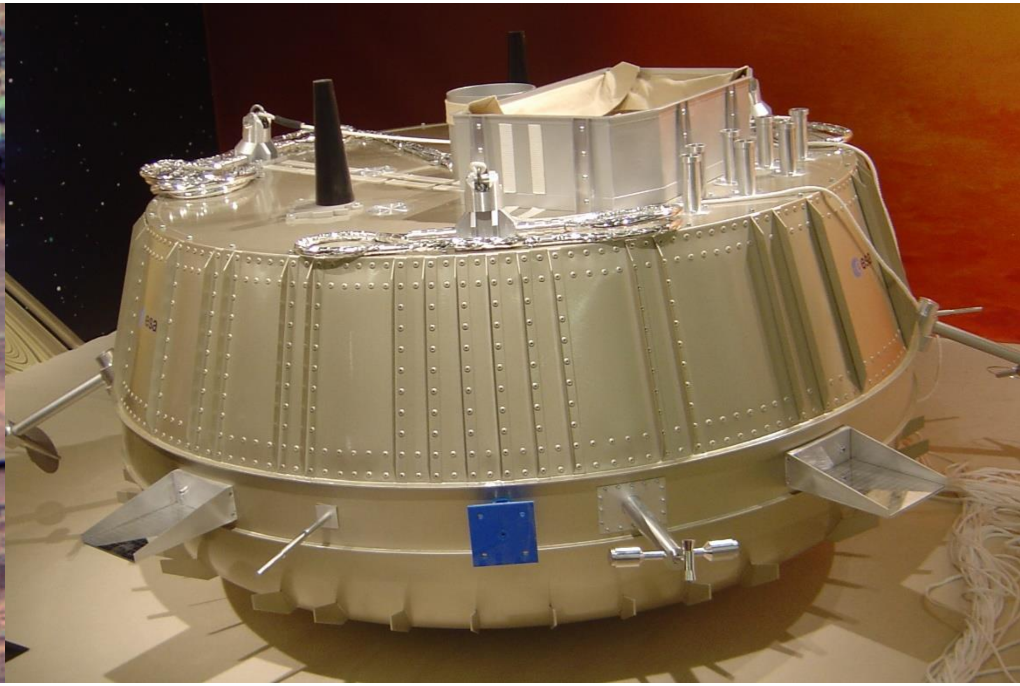
Galileo Probe 1989: Li/SO_2
~580 Wh
58 minutes



Sojourner Rover 1996: $Li/SOCl_2$
432 Wh
56 days (PV + battery)



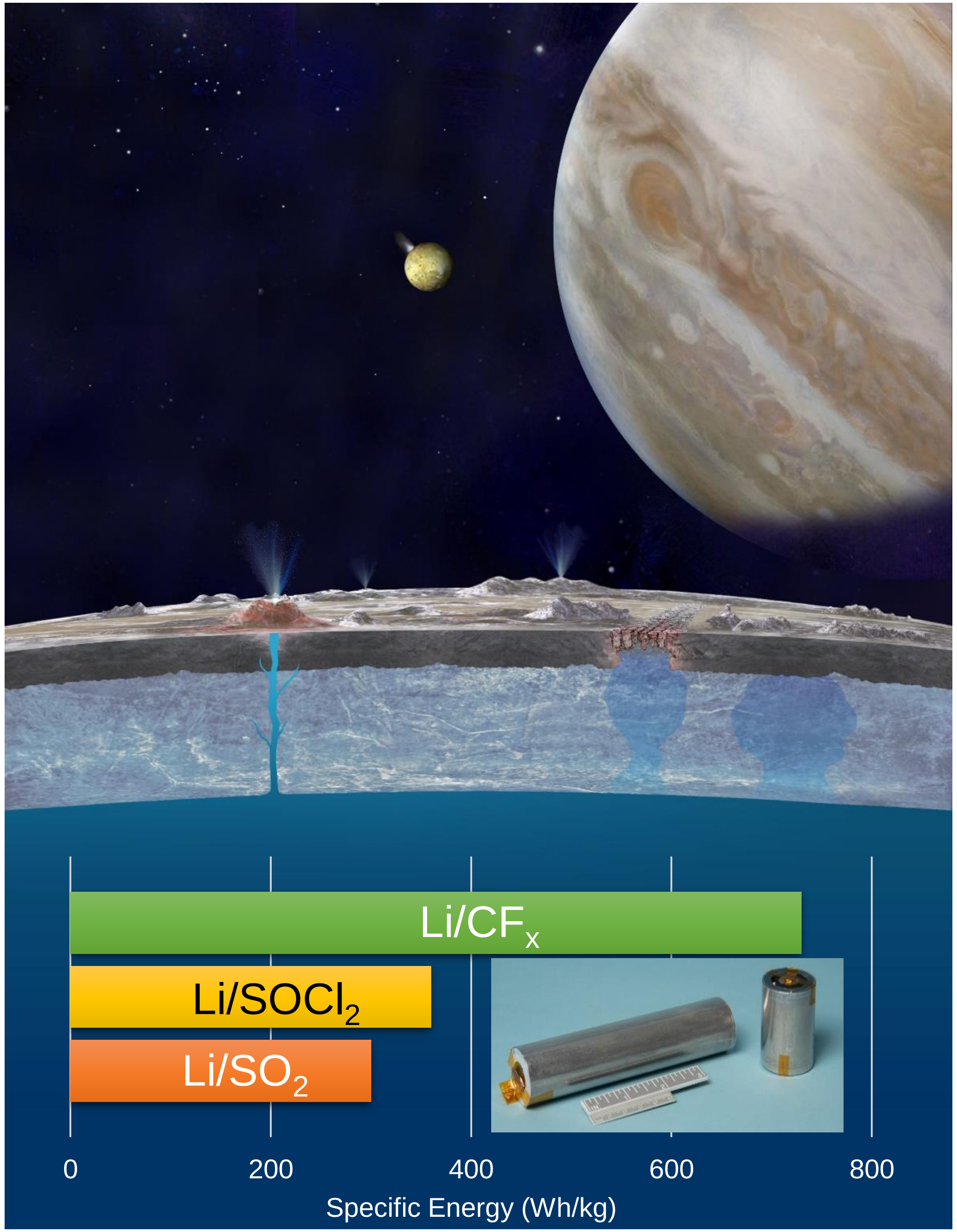
Huygens Probe 2004: Li/SO_2
~2700 Wh
153 minutes



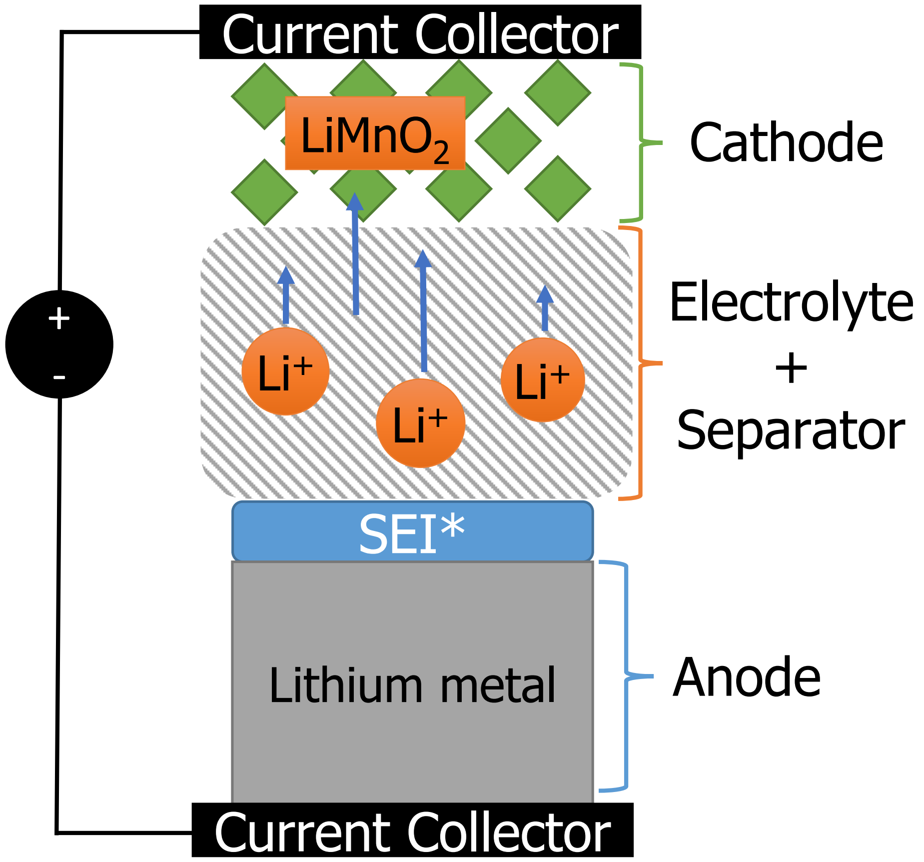
A Europa lander could require at least 480 hours of operation on battery power alone

Future Mission Needs

- Jupiter and Saturn's moons are attractive targets for future surface missions
- Extreme environments present significant challenges:
  - Europa: -171 °C
  - Enceladus: -198 °C
  - Titan: -180 °C
- Planetary protection requirements stringent for landers
- Specific energy must be high
- **Long duration missions in harsh environments demand new battery technology**



Battery basics



Lithium cell during discharge

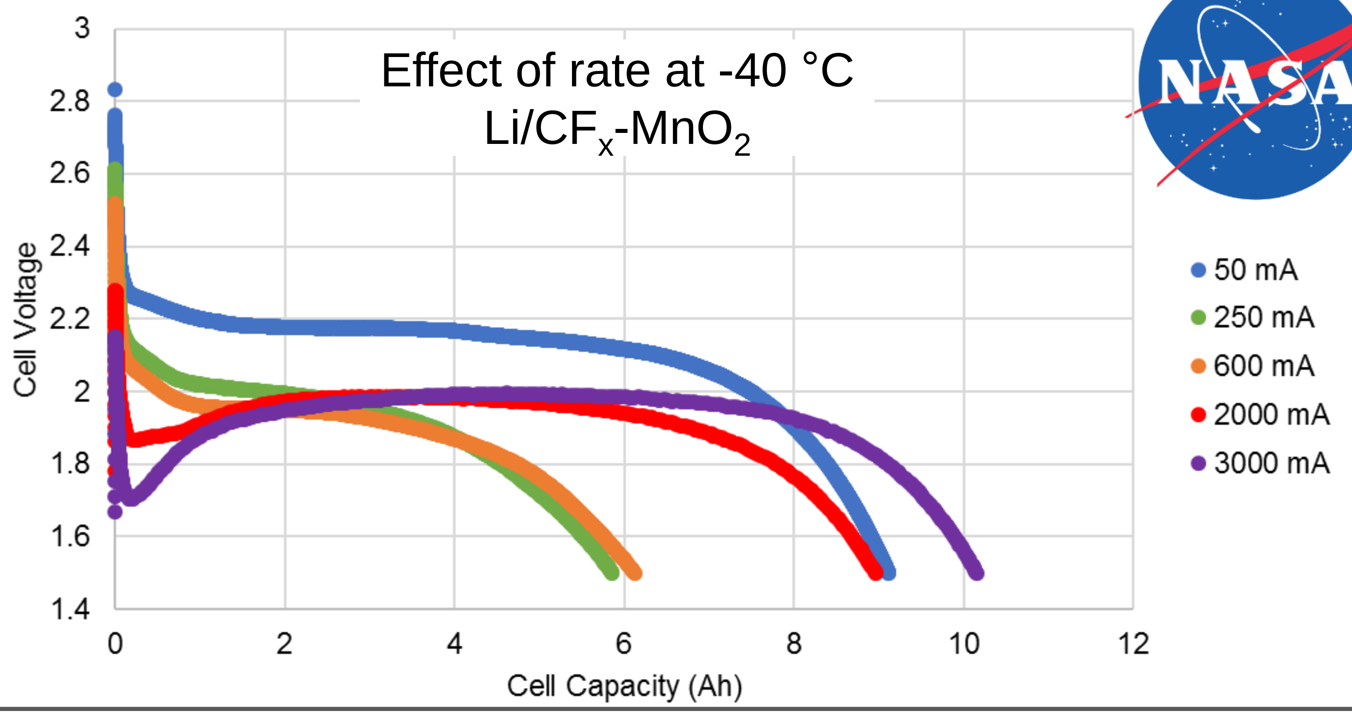
Metrics for comparison:

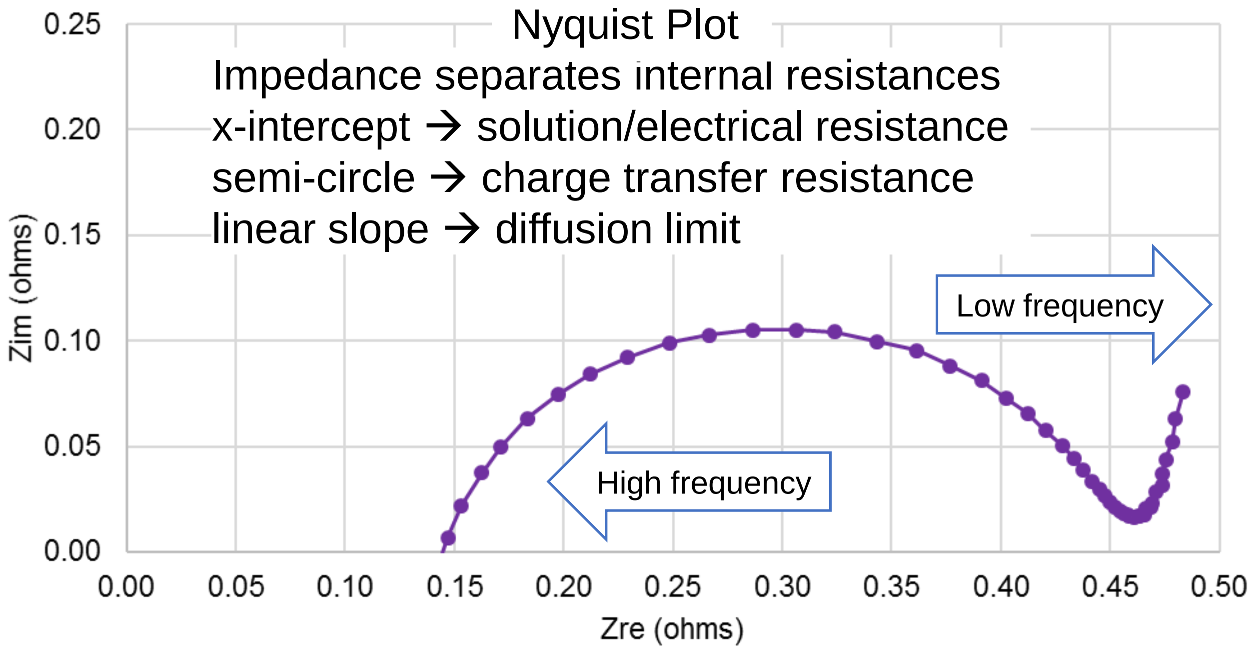
- Capacity (amp-hours)
- Voltage
- Energy (watt-hours)
- **Specific Energy (watt-hours/kg)**
- Volumetric energy density (watt-hours/L)
- Rate capability (c-rate)
- Low/high temperature performance
- Self discharge

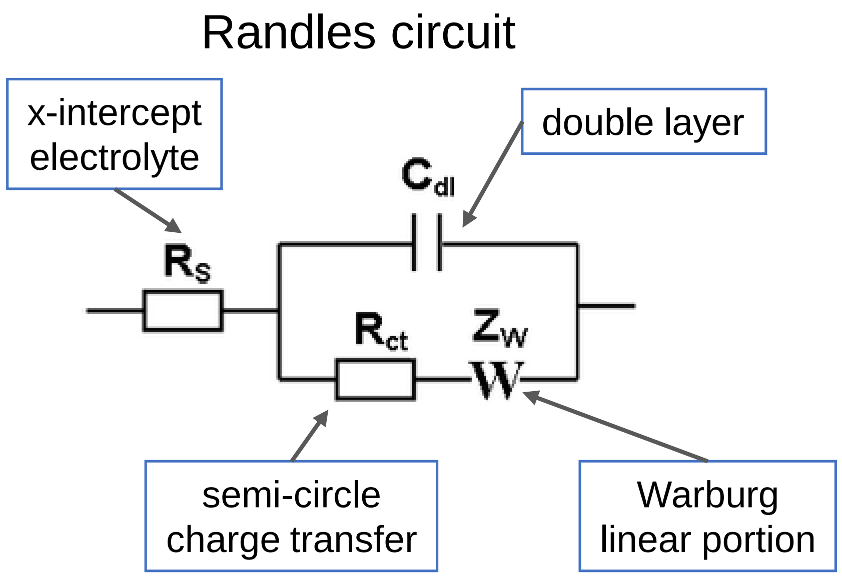
* SEI = Solid Electrolyte Interphase, which protects the electrolyte from the highly reactive electrodes

Testing methods

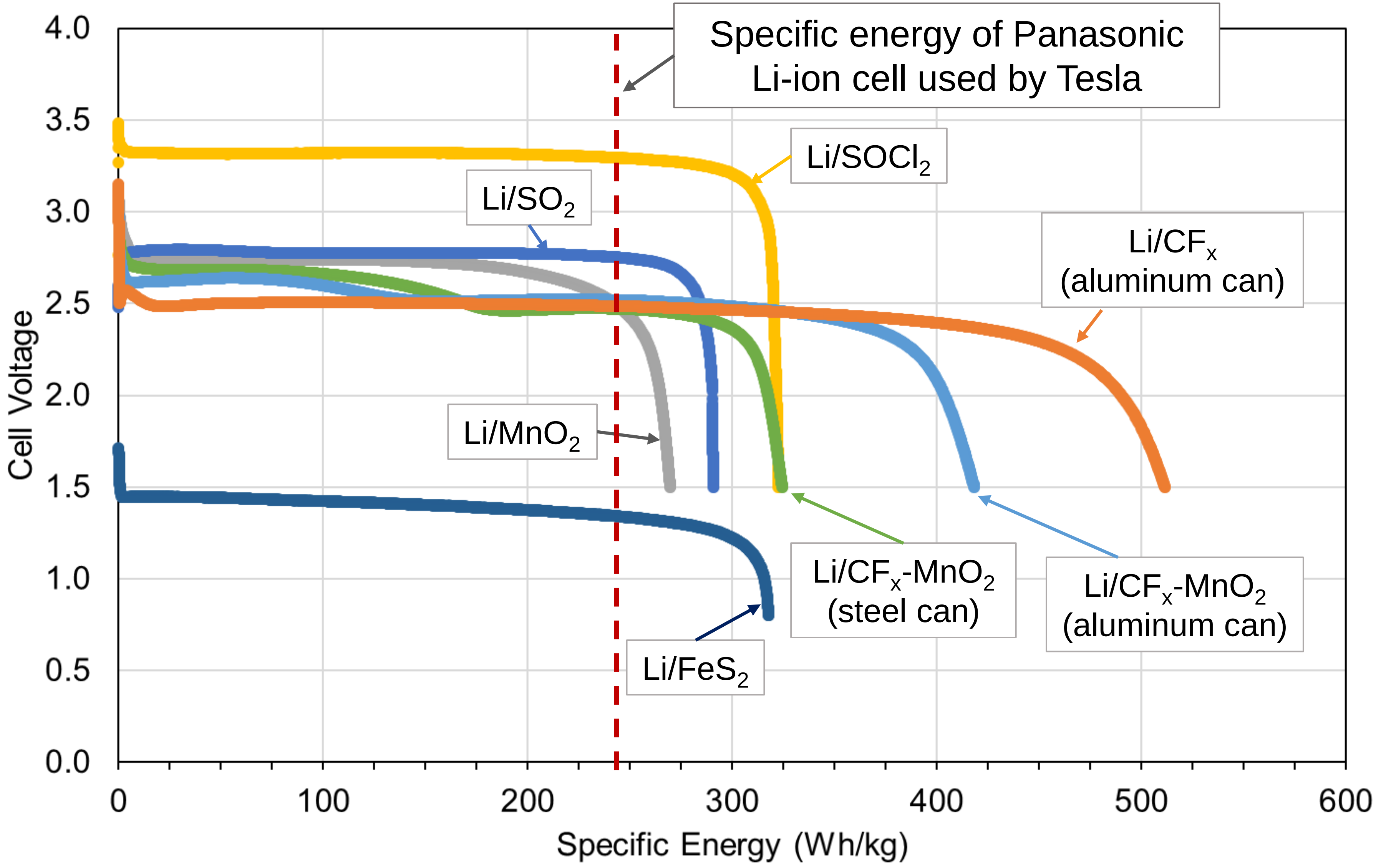
- Discharge/cycling performance
  - Rate (50, 250 and 600 mA)
  - Temperature (-40 to +21 °C)
- Impedance analysis
  - Apply range of frequencies to cell
  - “static” conditions





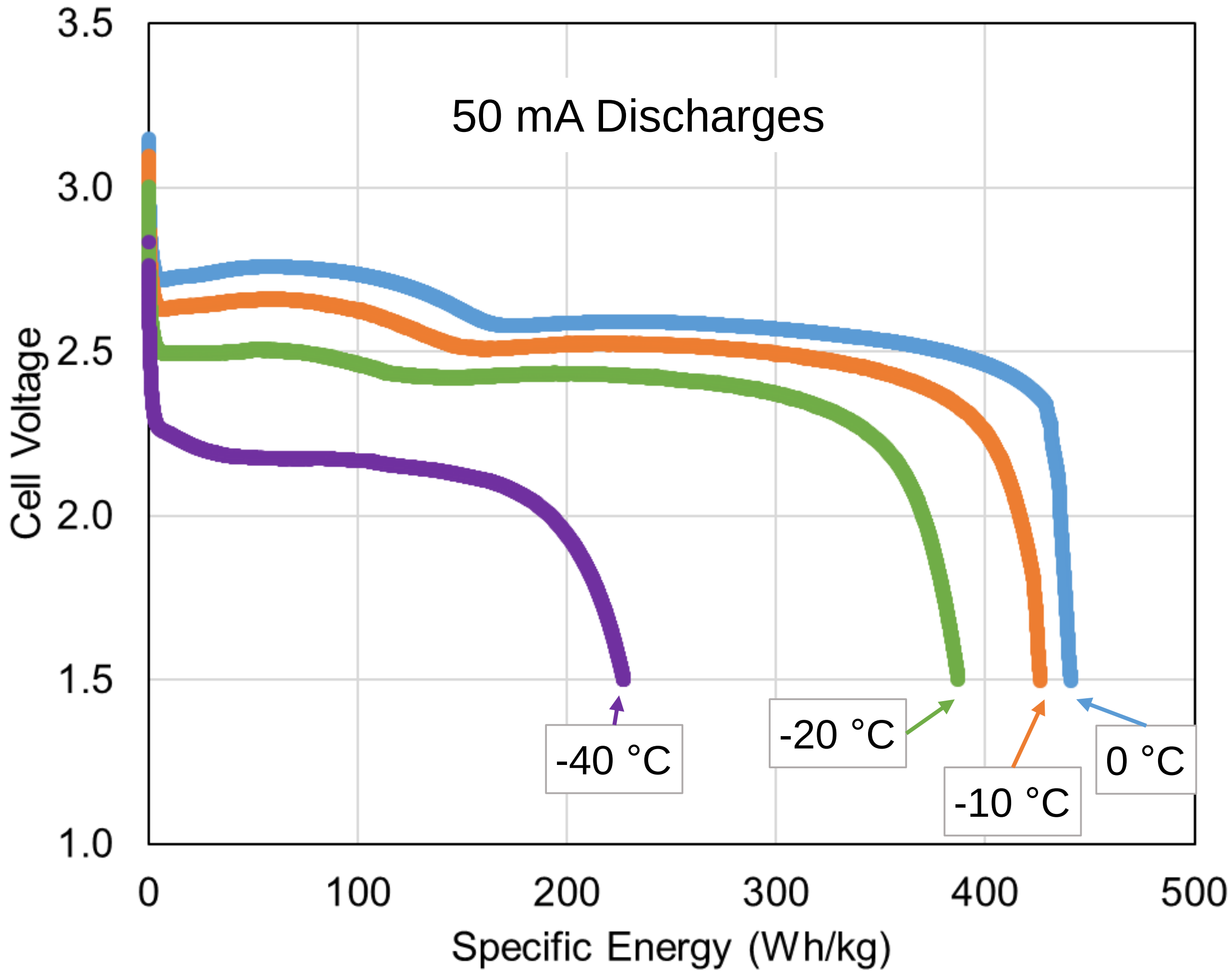


D-size Lithium Primary Battery Comparison



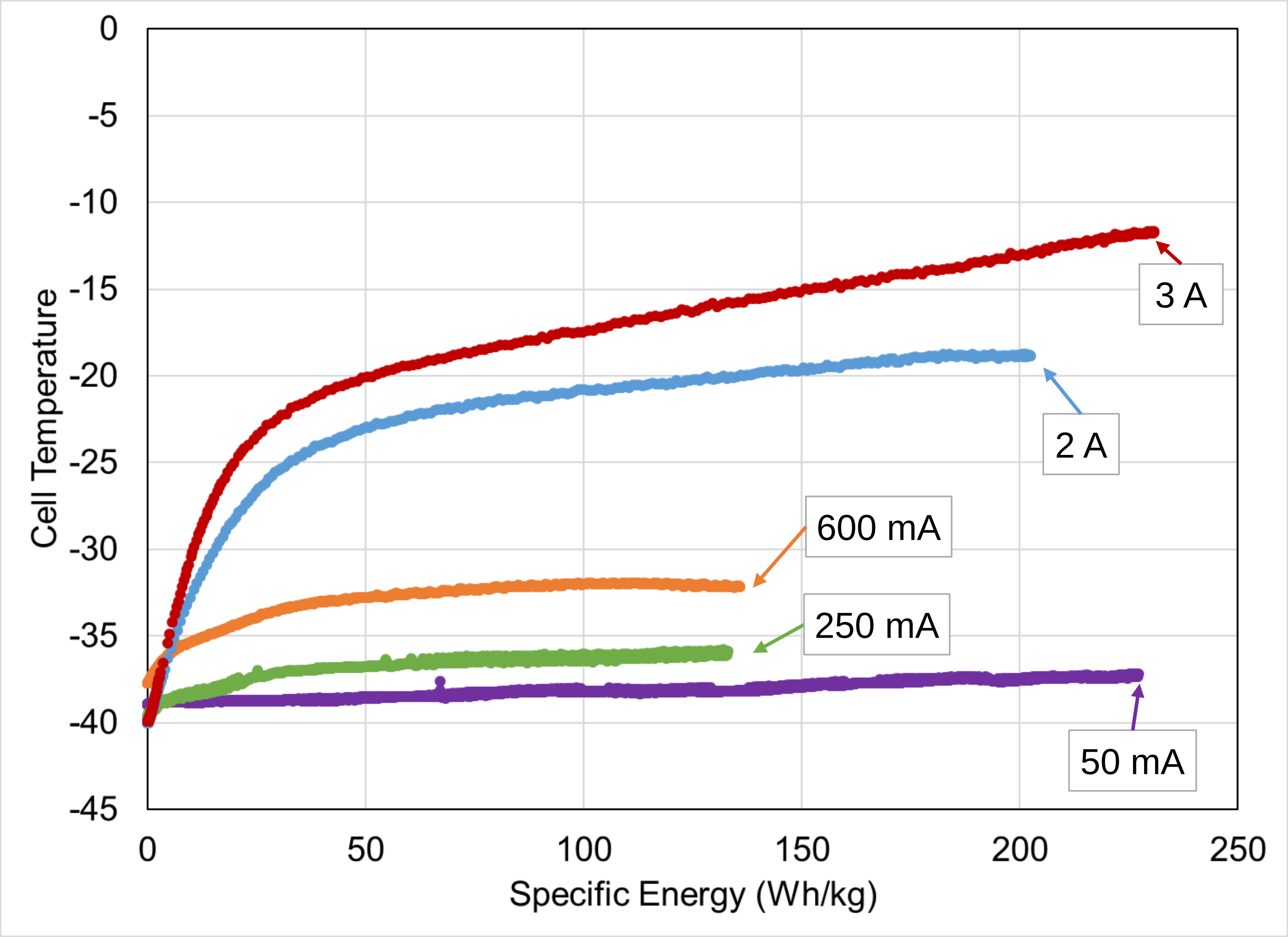
- Discharged at the same condition
- 0 °C, 250 mA
- Li/FeS$_2$ discharged at 100 mA due to size (AA instead of D)
- 2 Li/FeS$_2$ cells could be connected in series to provide comparable voltage

Li/CF$_x$-MnO$_2$ Temperature Dependence



Specific energy falls sharply below -20 °C

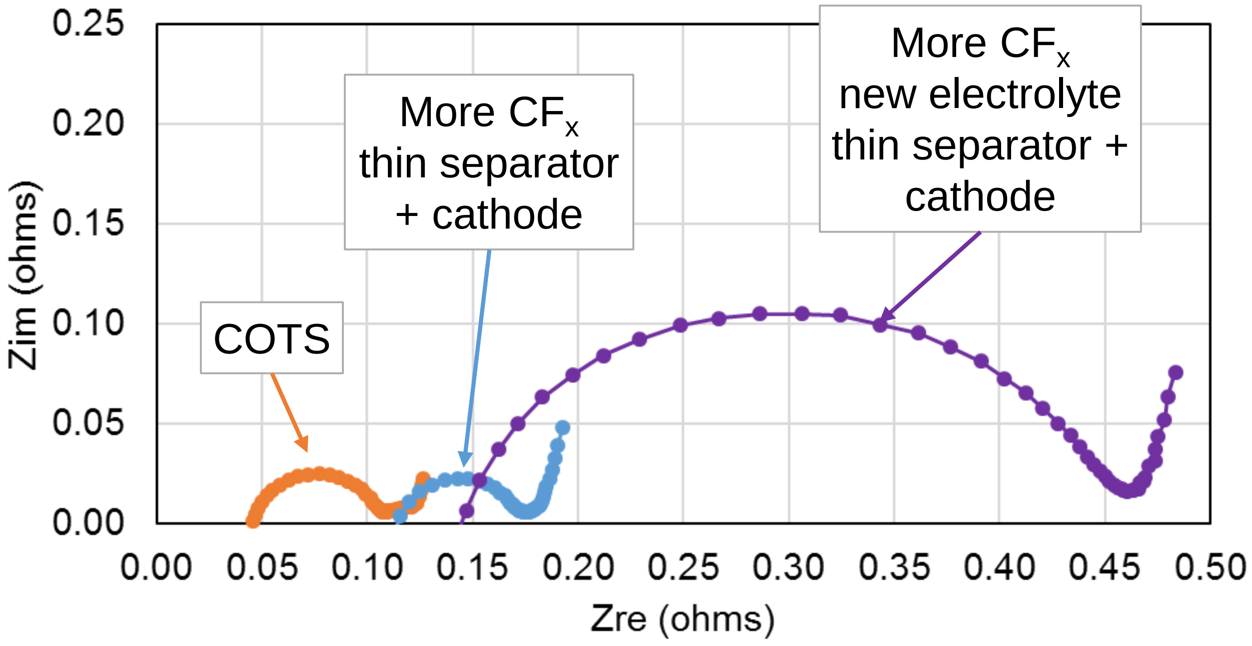
Li/CF_x-MnO_2 Discharge Rate at -40 °C

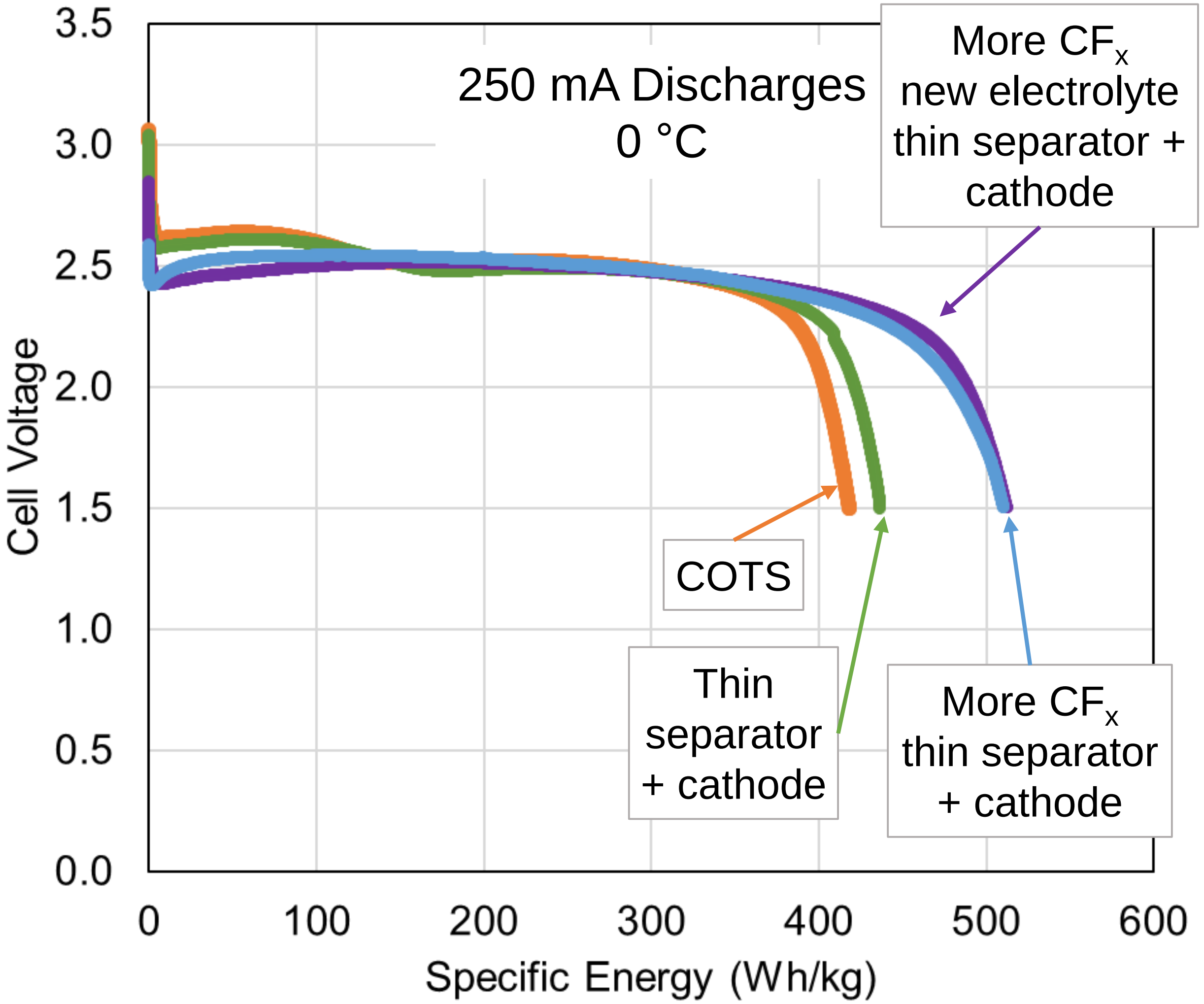


Higher rates lead to more heat

Eagle-Picher improved cells

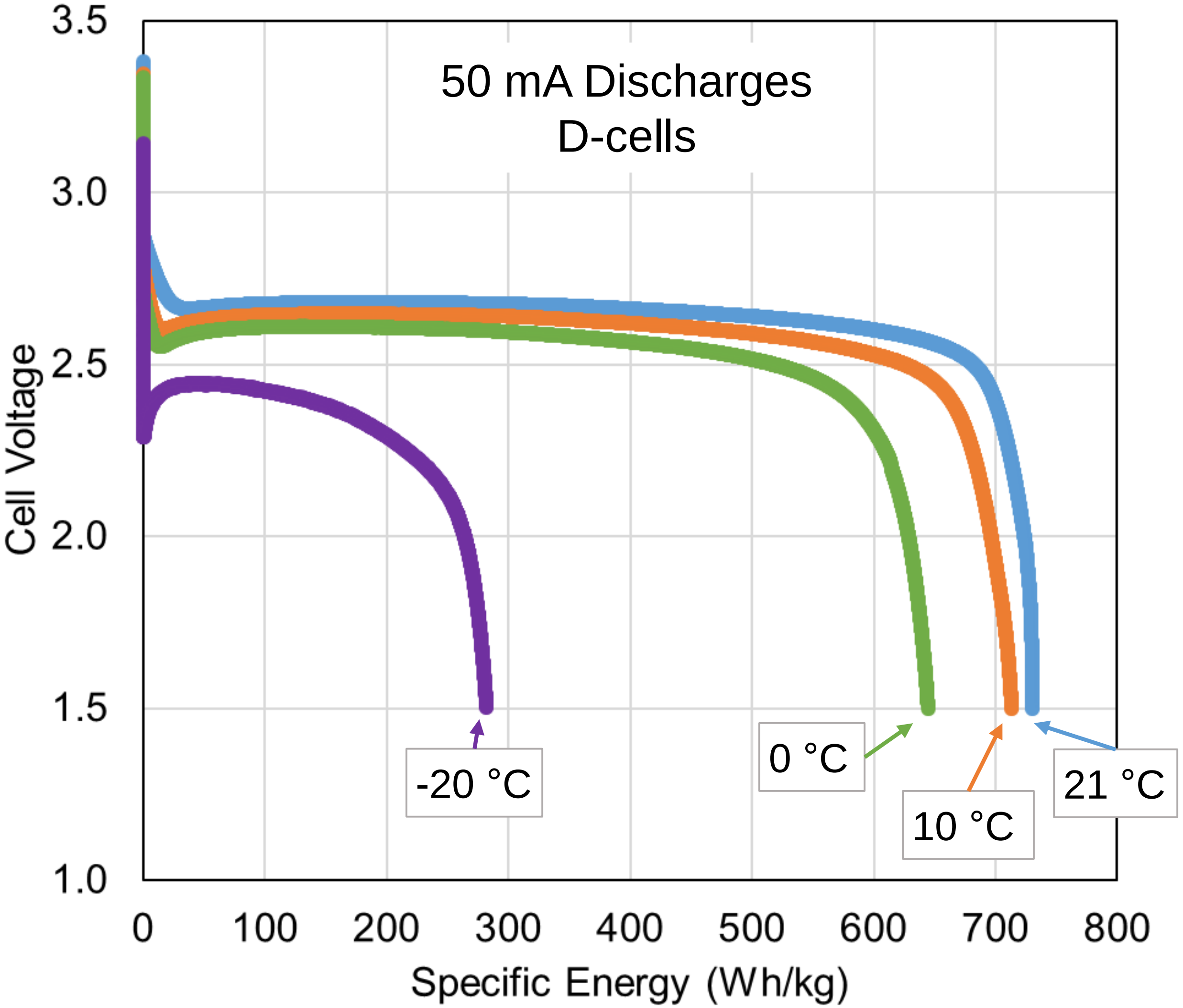
low temperature, low rate targeted





More CF_x → increased cell resistance
New electrolyte → increased cell resistance

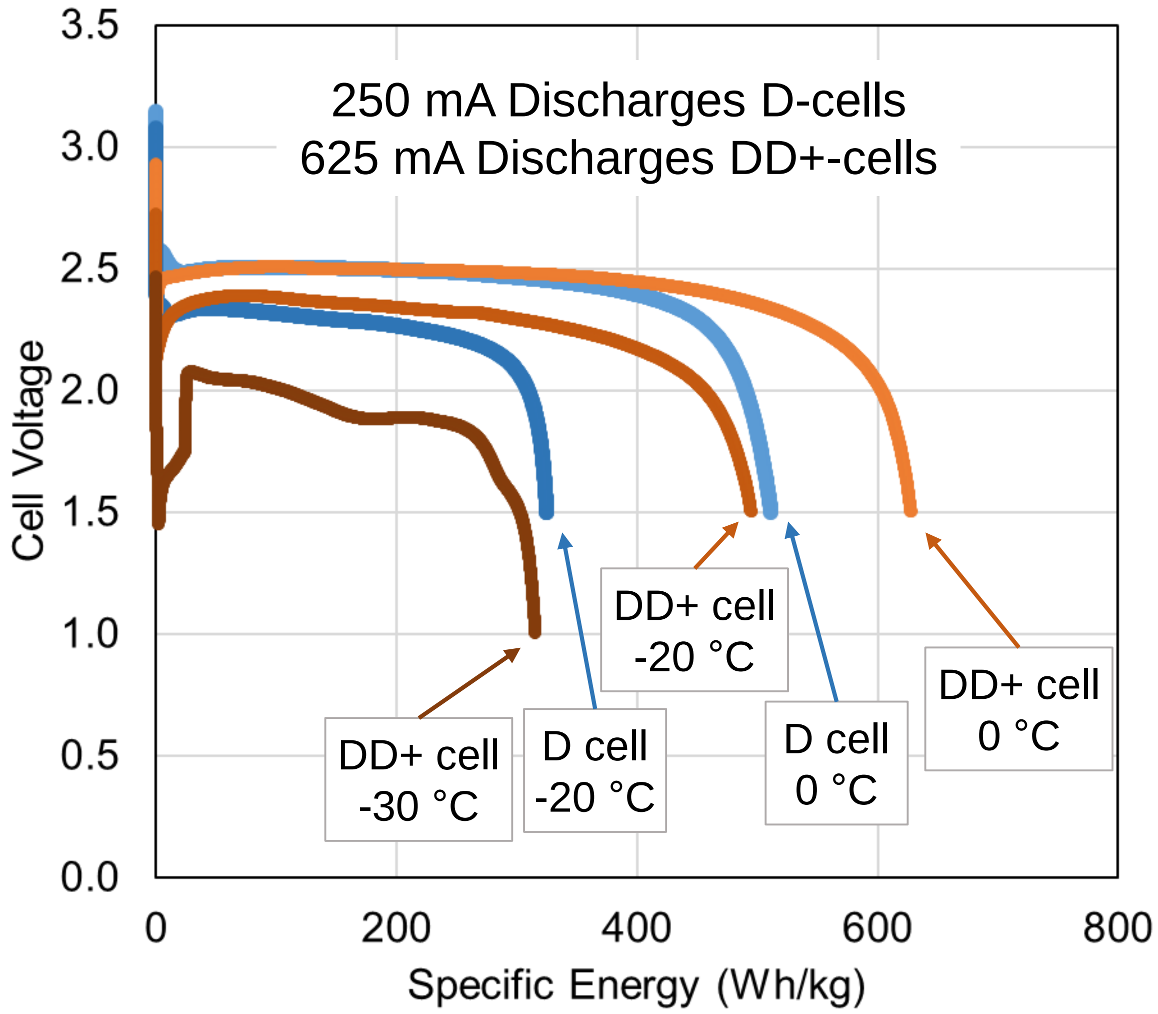
Li/CF_x Performance

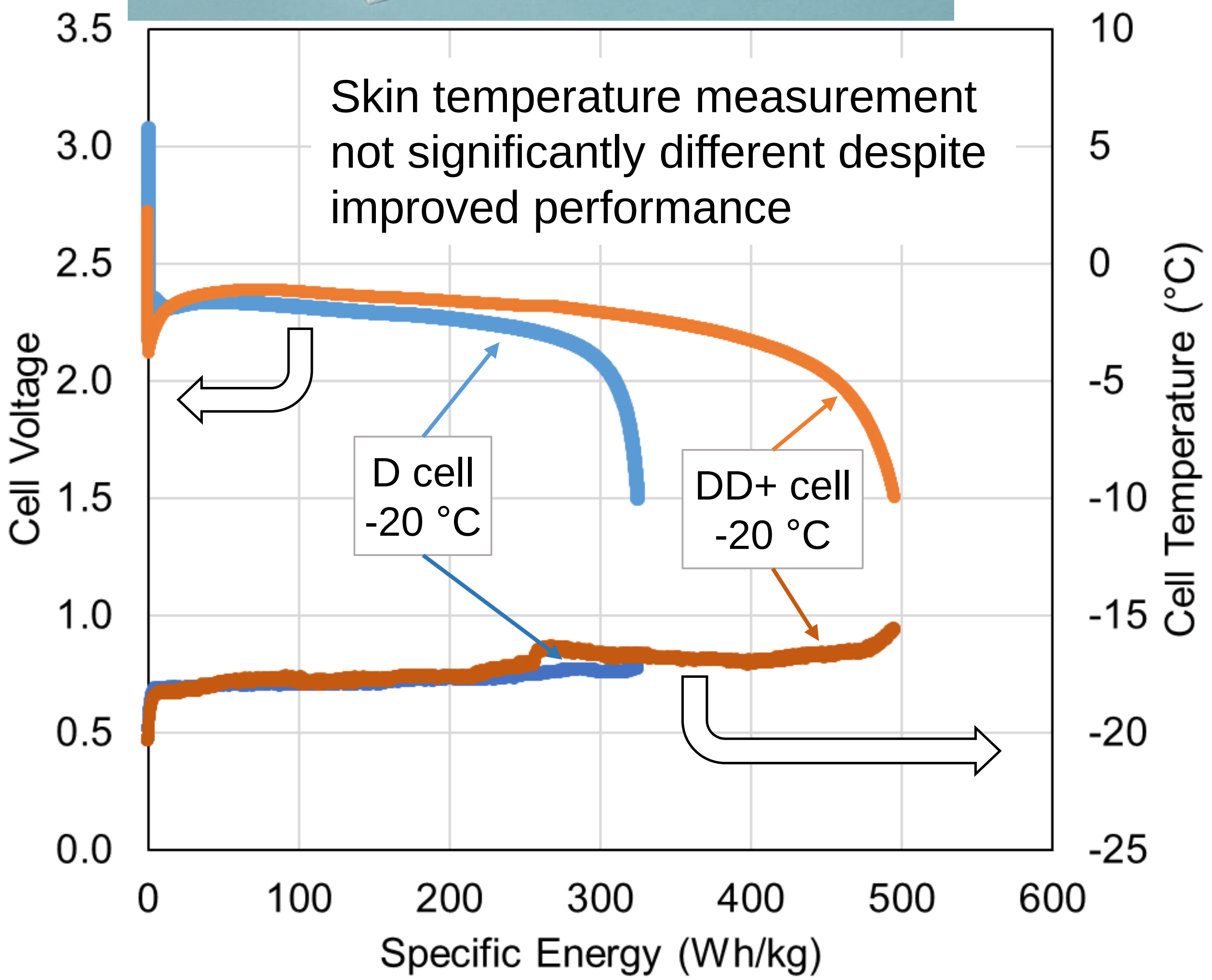


Highest Specific Energy at 50 mA, 21 °C: **730 Wh/kg**

Li/CF_x DD+ cell format

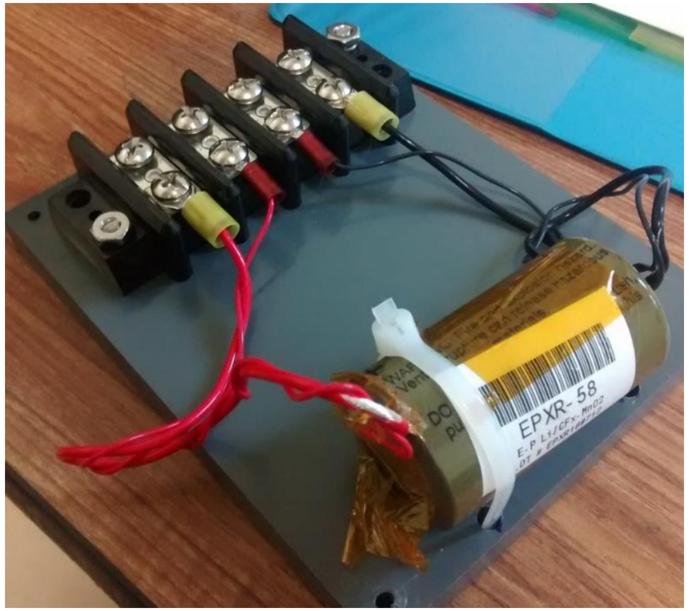
DD+ format improves low temperature performance

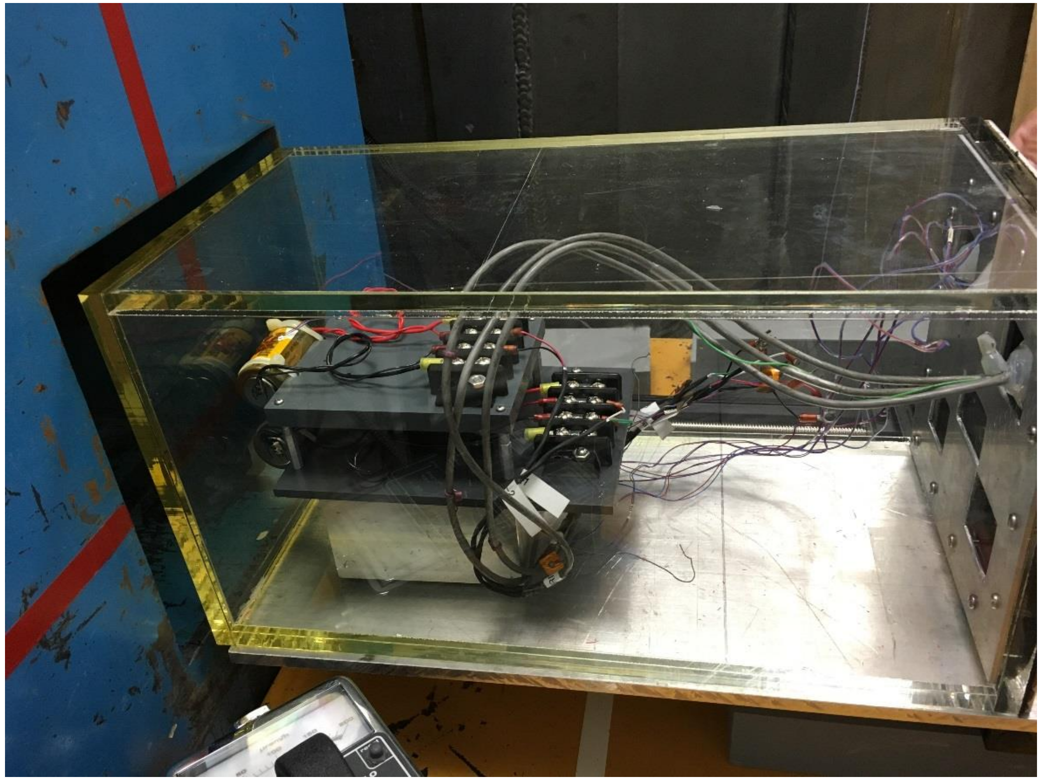




Radiation Testing

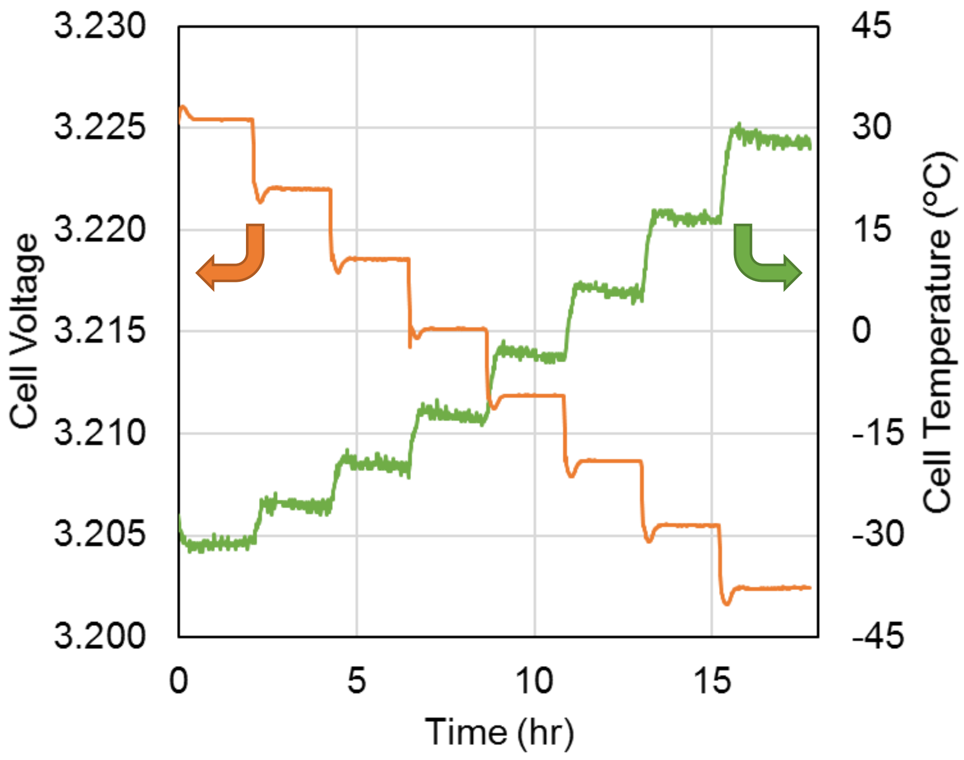
- Long cruise time 6~7 years
- Possible planetary protection protocol
- Eagle-Picher Li/CF_x-MnO_2 hybrid COTS cells
- JPL high dose rate ^{60}Co source
  - 1.3 MeV gamma rays
  - ~200 rad/s
  - 1 MRad up to 15 MRad

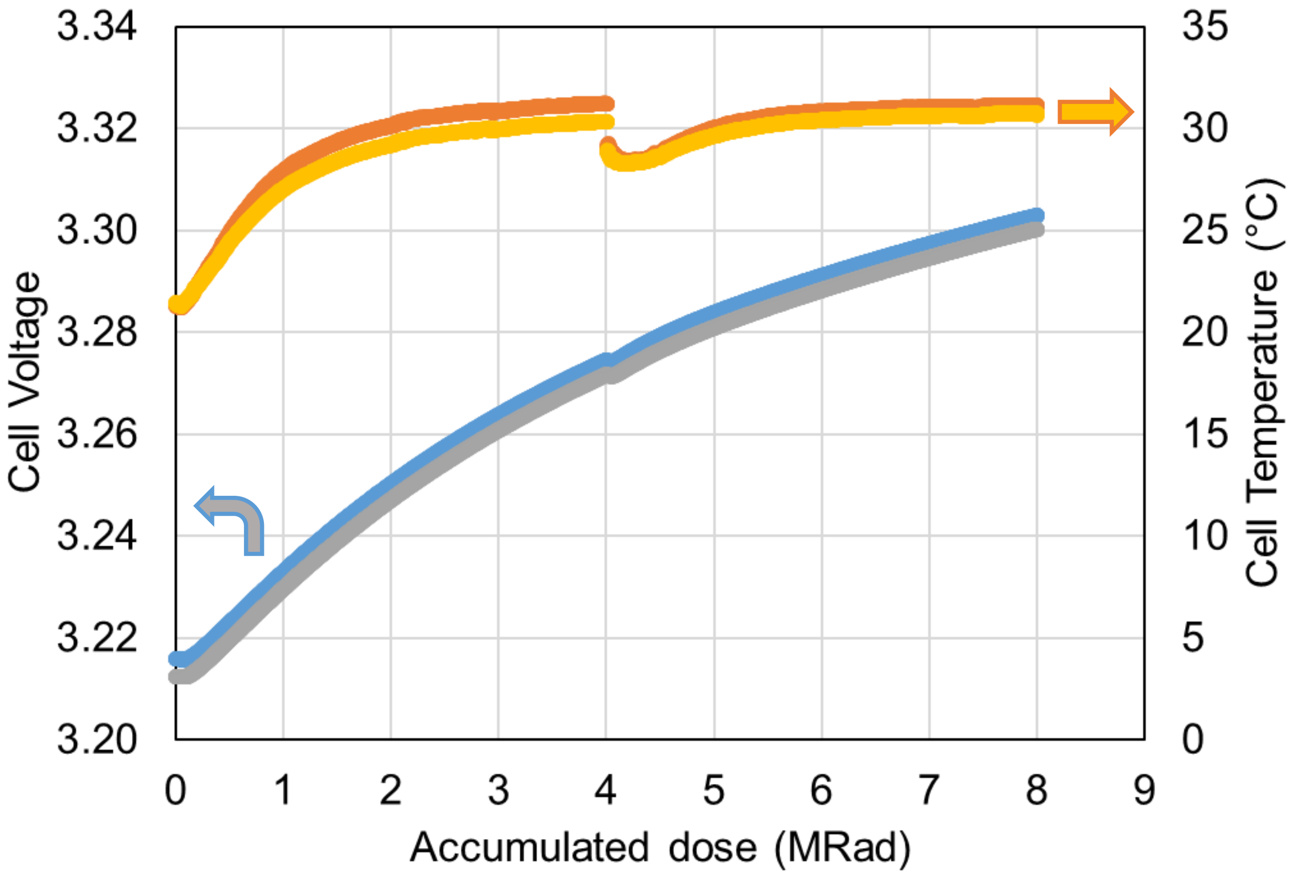




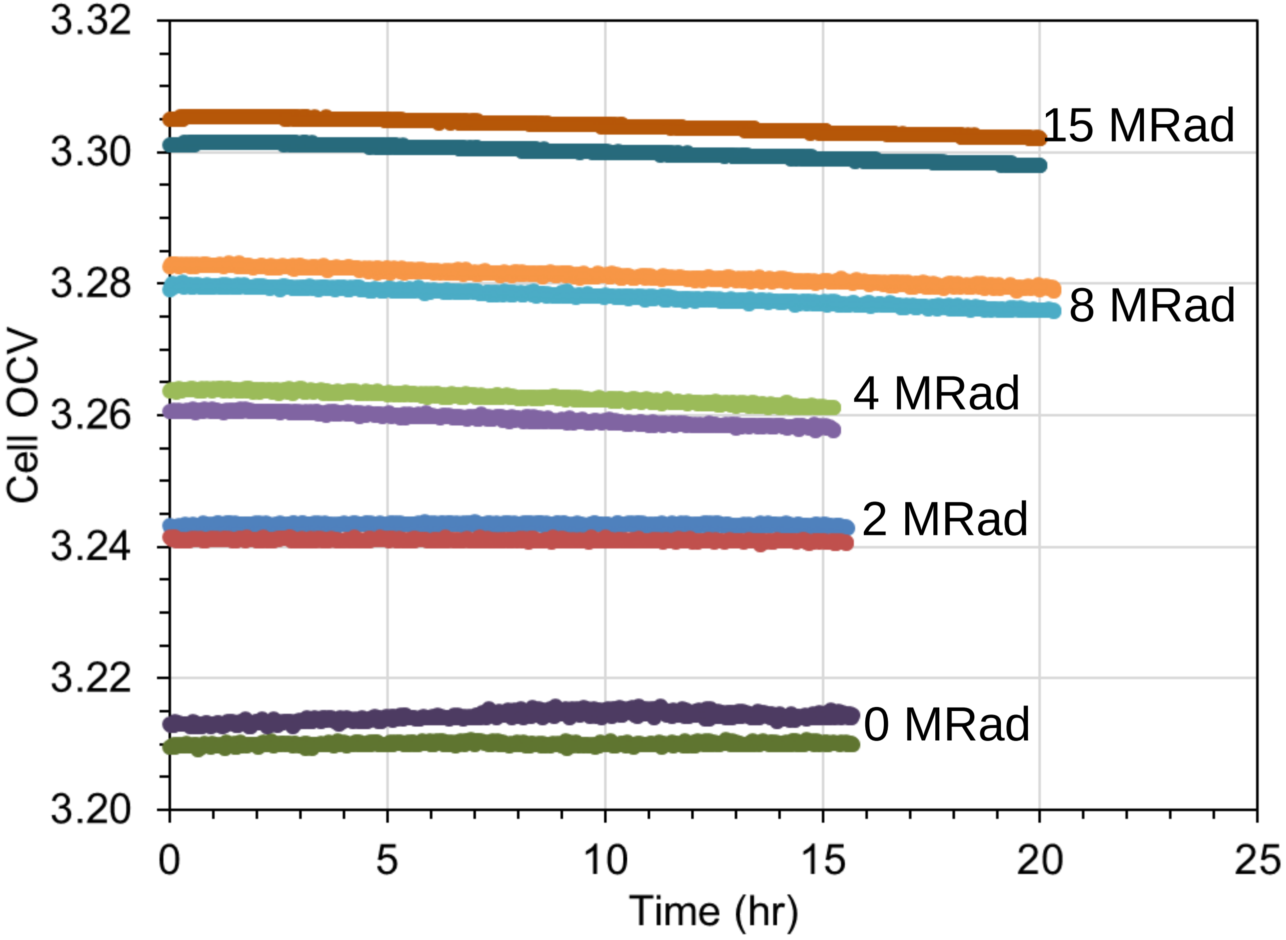
Li/CF_x-MnO_2 cell voltages increase during radiation exposure

Temperature rise does not correlate with voltage increase

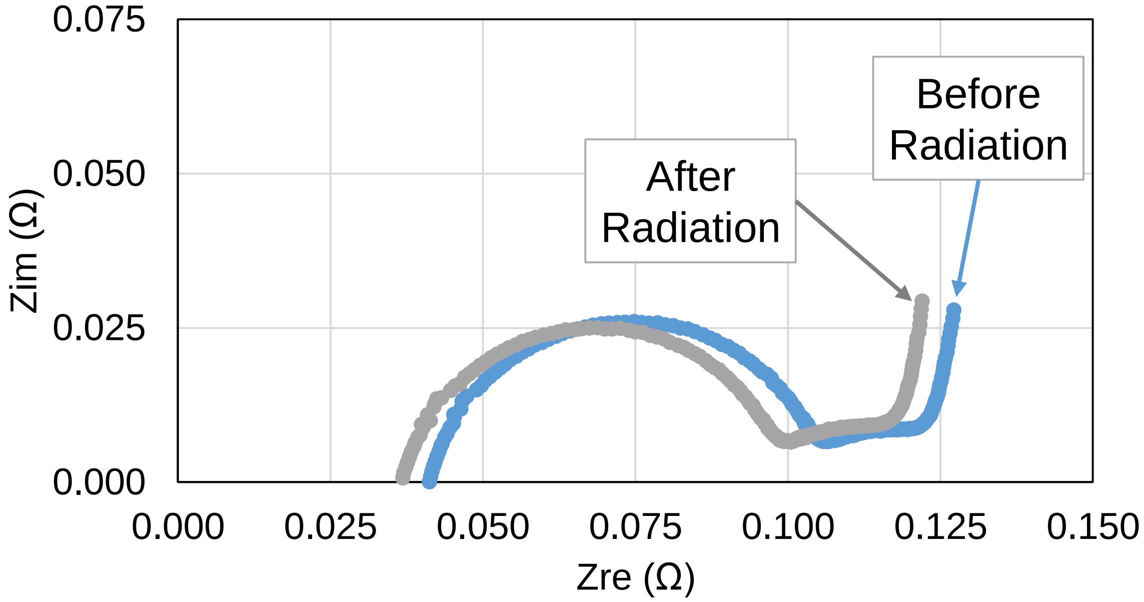




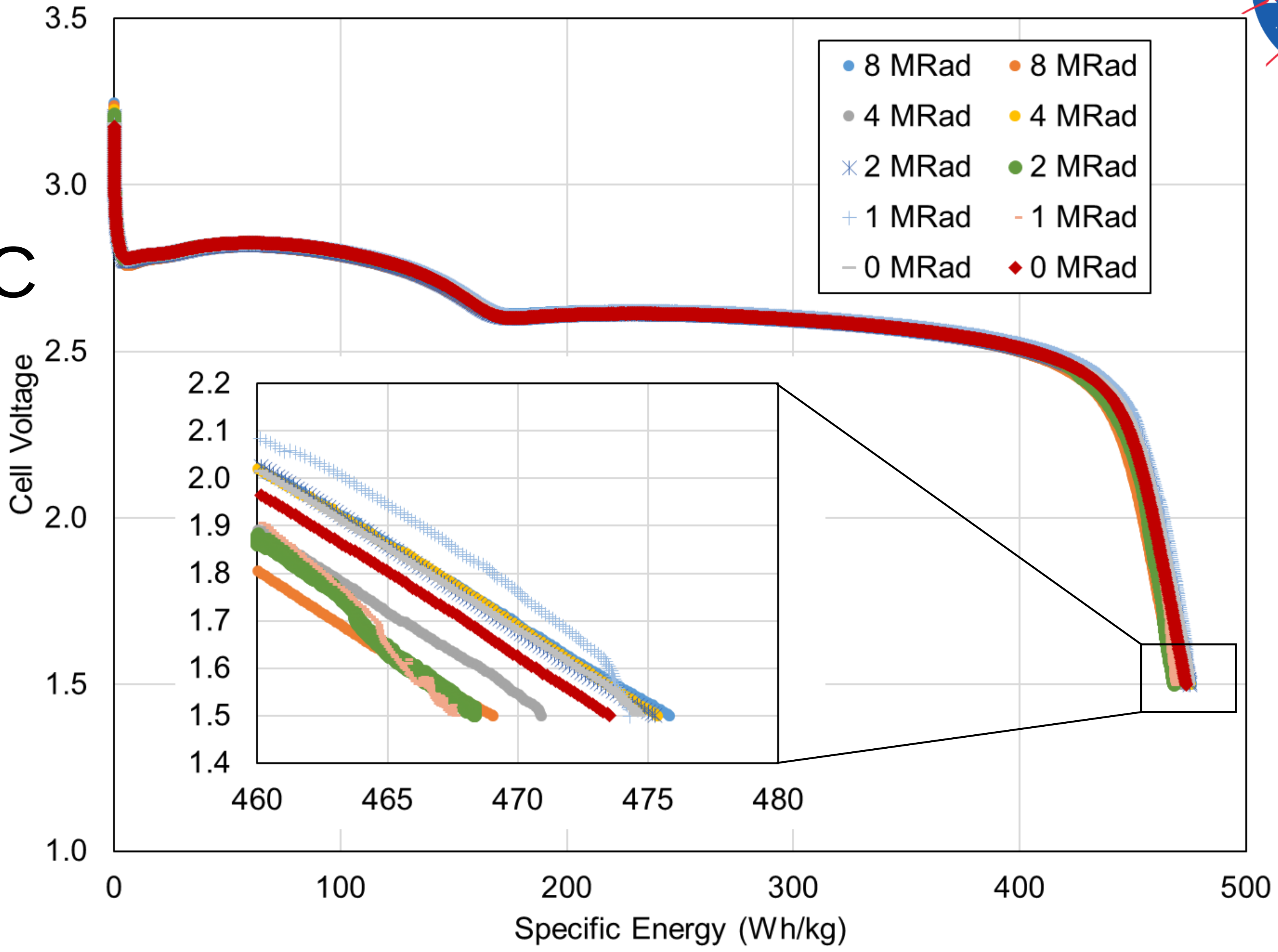
Voltage Slowly Relaxes Li/CF_x-MnO_2 Cells



- OCV monitored for >15 hours
- Linear regression analysis shows a slight voltage drop (**0.18 to 0.2 mV/hr**) for higher dose cells (4, 8, 15 MRad)
- No change in impedance after radiation



Li/CF_x-MnO_2 Radiation cell discharges at 250 mA, 21 °C

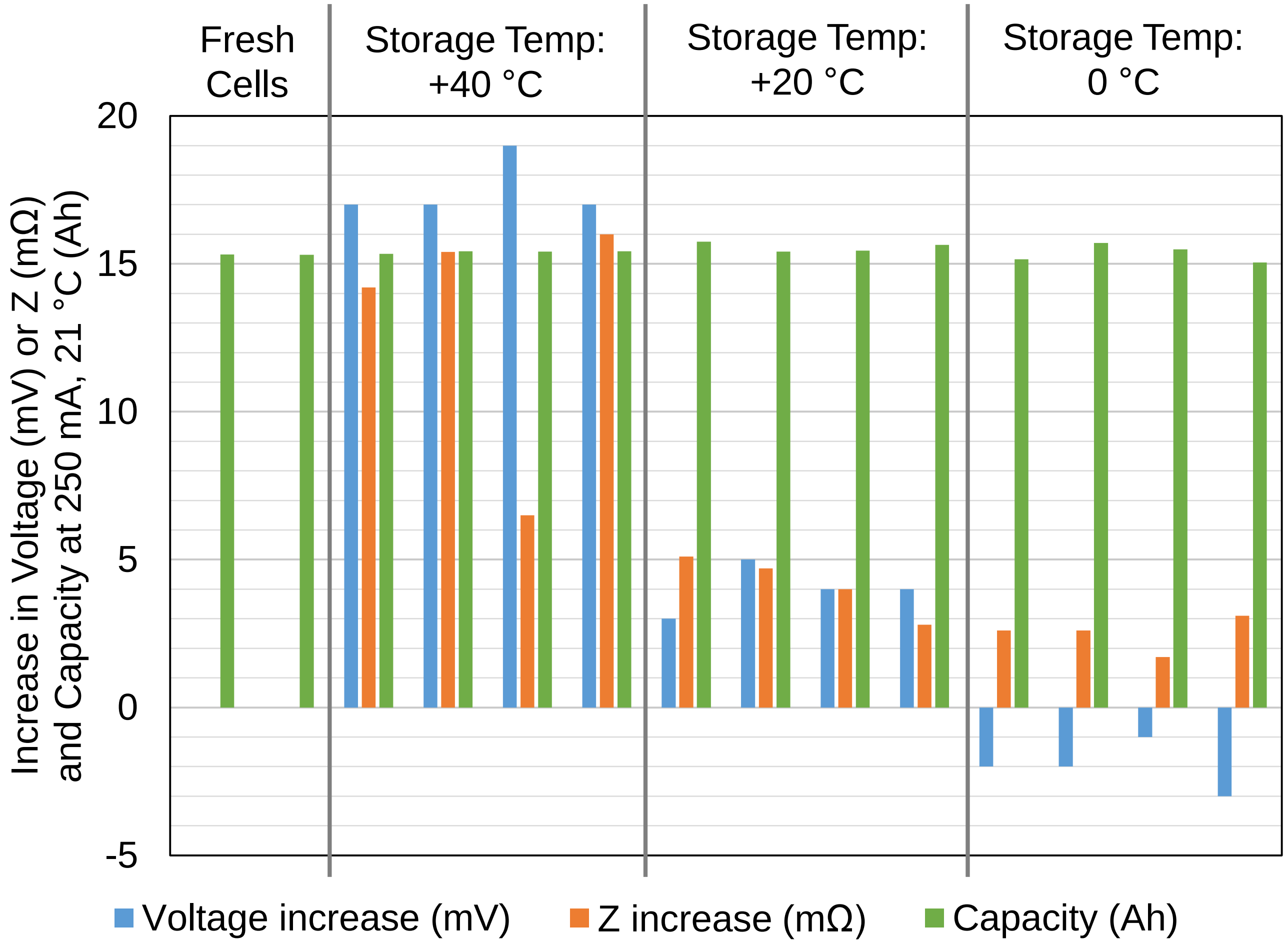


- ☑ No negative effects have been observed on specific energy
- ☑ May be useful for planetary protection

Storage testing Li/CF_x-MnO_2

- Storage at 3 temperatures
  - 40 °C
  - 20 °C
  - 0 °C
- Pull cells out after 3 months, then every 6 months for 3 years
- Check impedance, voltage change and discharge performance

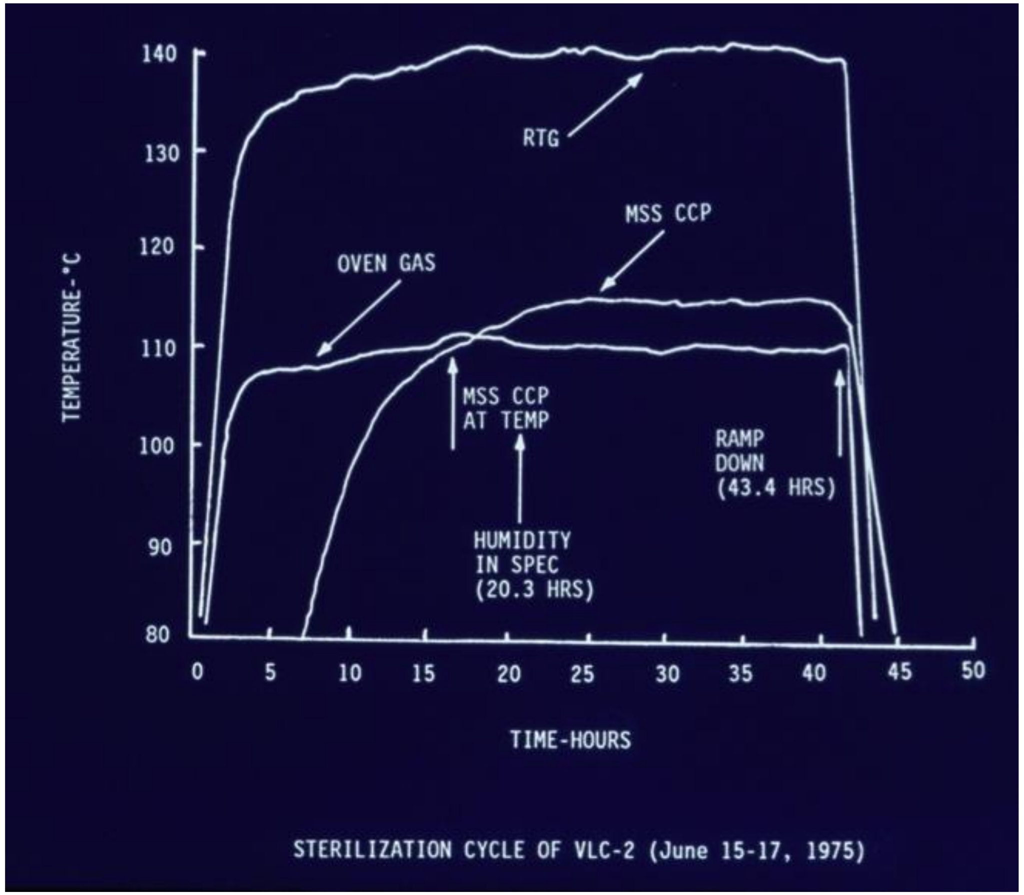
3 Month Storage Results
No impact on capacity



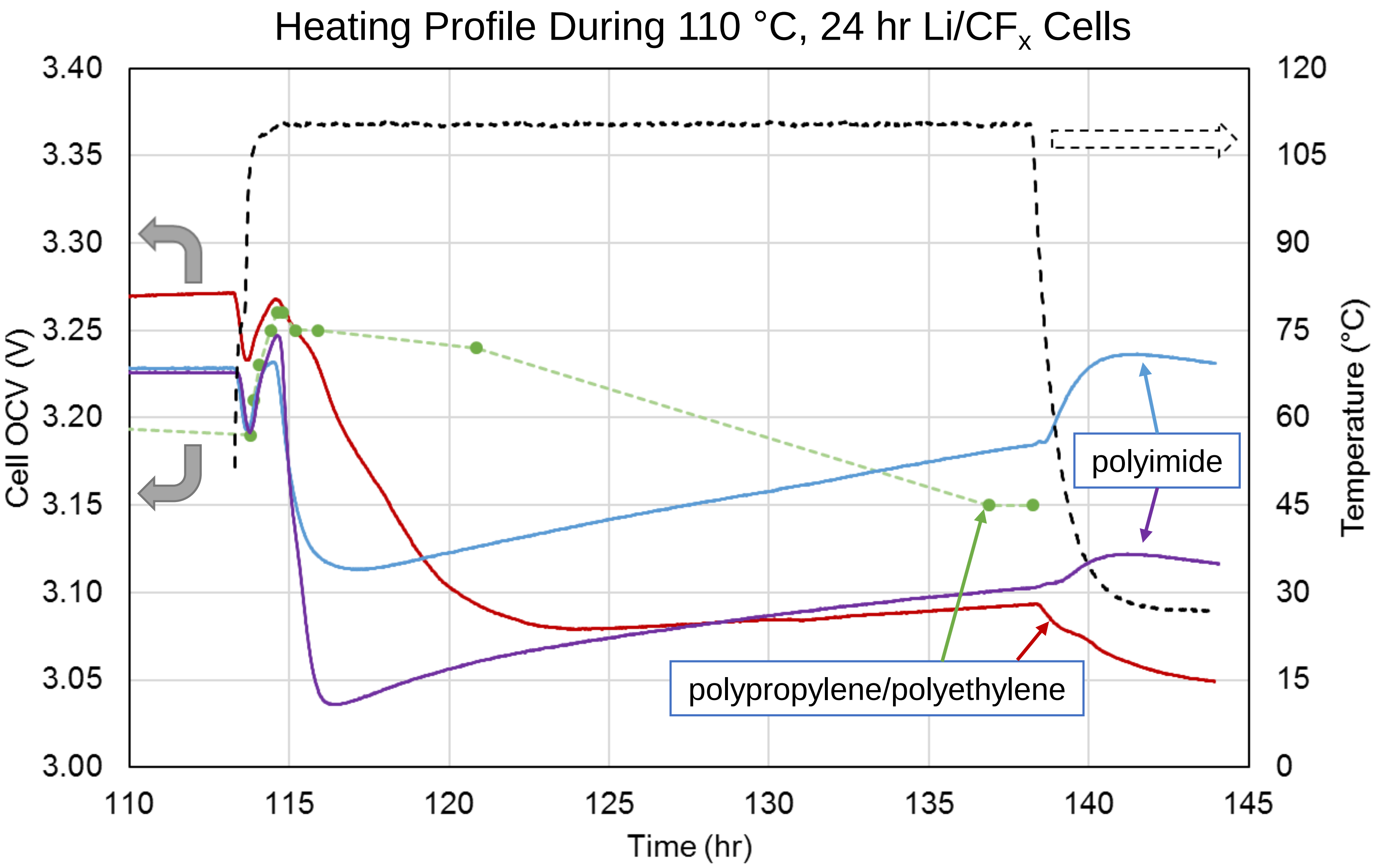
Experimental Cell Dry Heat Microbial Reduction (DHMR)

- Planetary protection requirements
  - Heat cells to reduce microbial content
- Heat cells to 110-170 °C
  - Minimum of 110 °C based on Viking
  - Lithium melts at 180 °C
  - Cells typically rated to 80 °C
- Discharge to understand effects
  - Room temp discharge to measure capacity
  - Low temperature to measure increased resistance

Viking DHMR

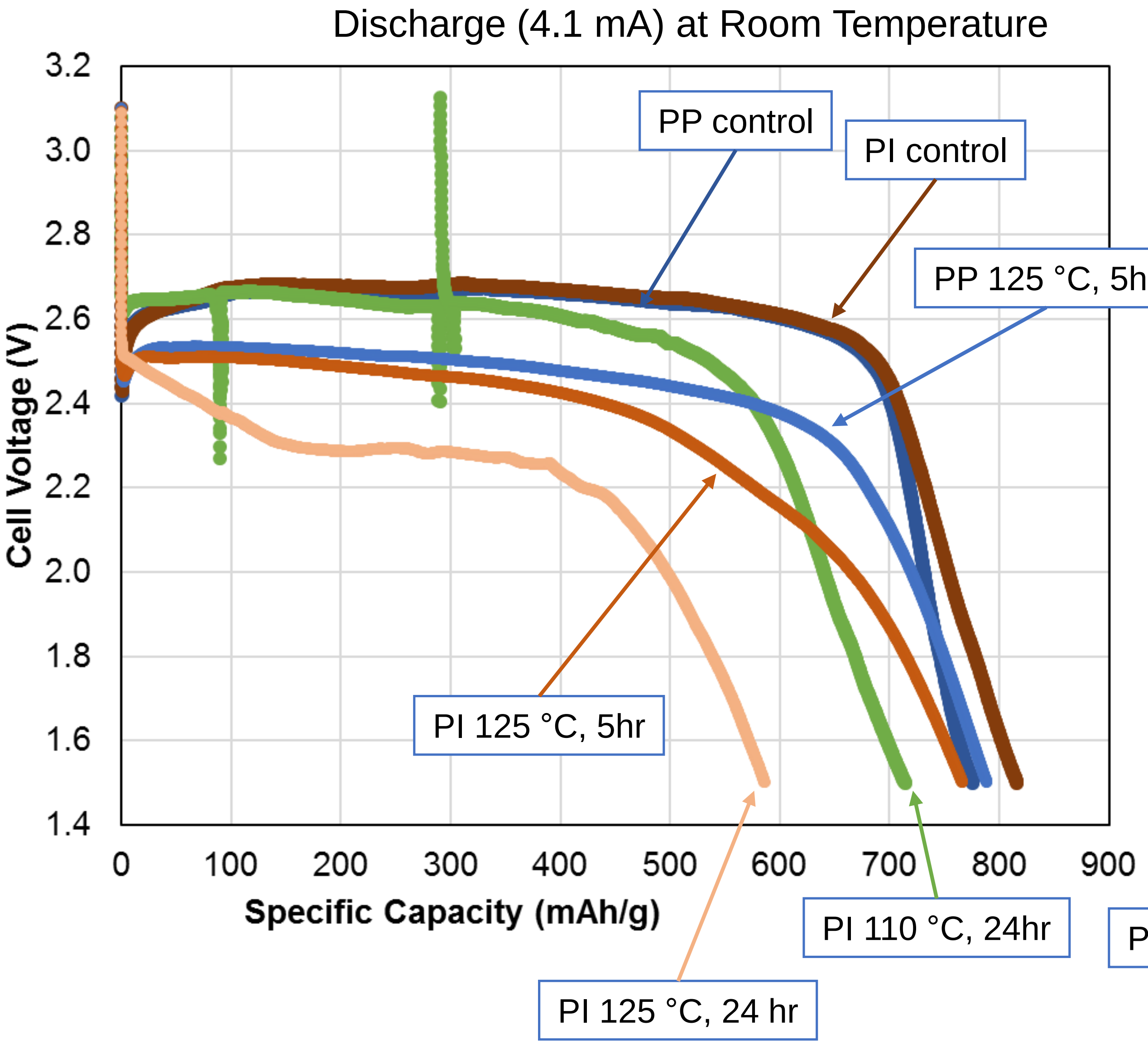


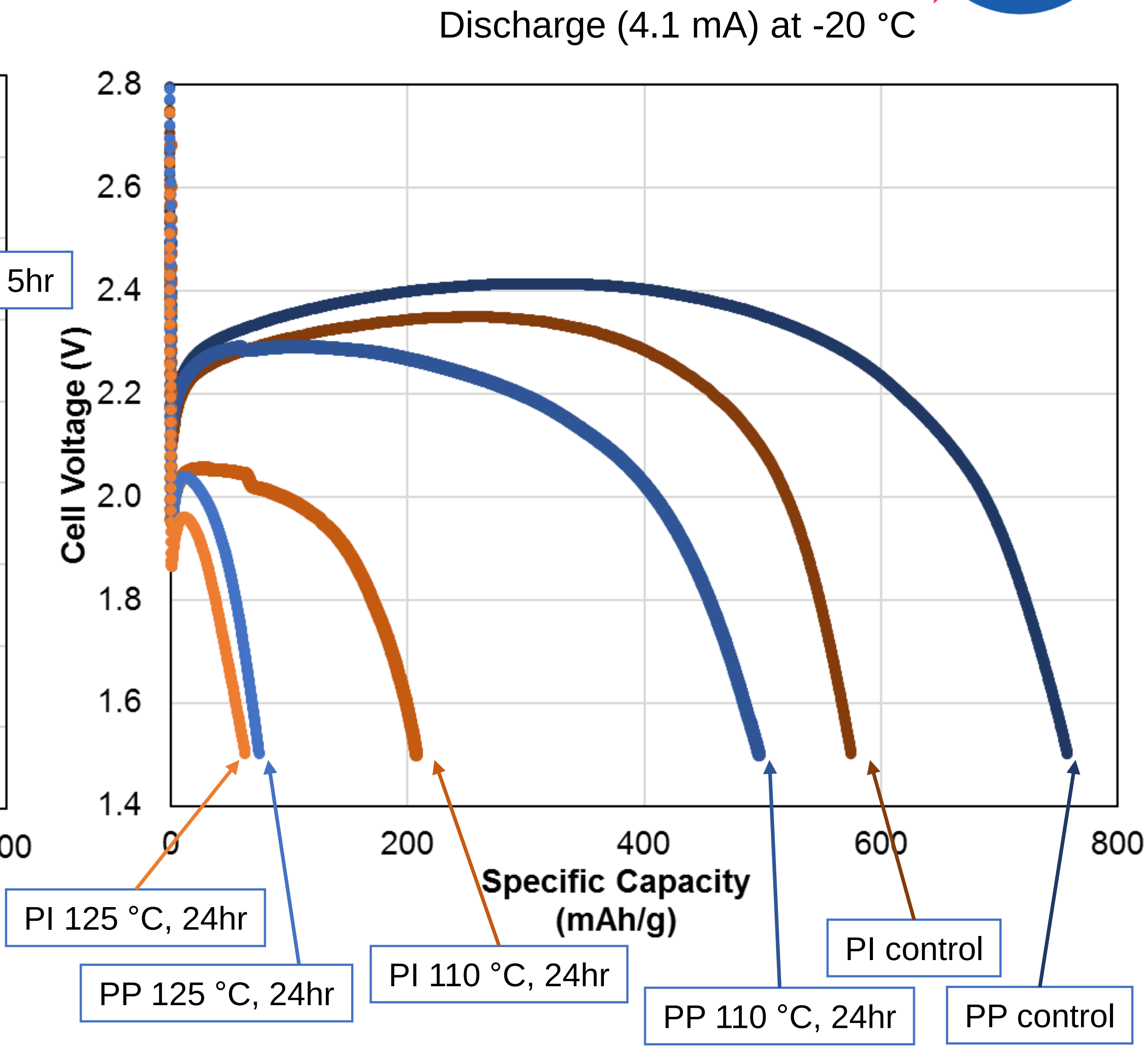
Dry Heat Microbial Reduction (DHMR) Evaluation for Planetary Protection



Discharge Performance After DHMR

☒ DHMR does not look promising for Li/CF_x cells



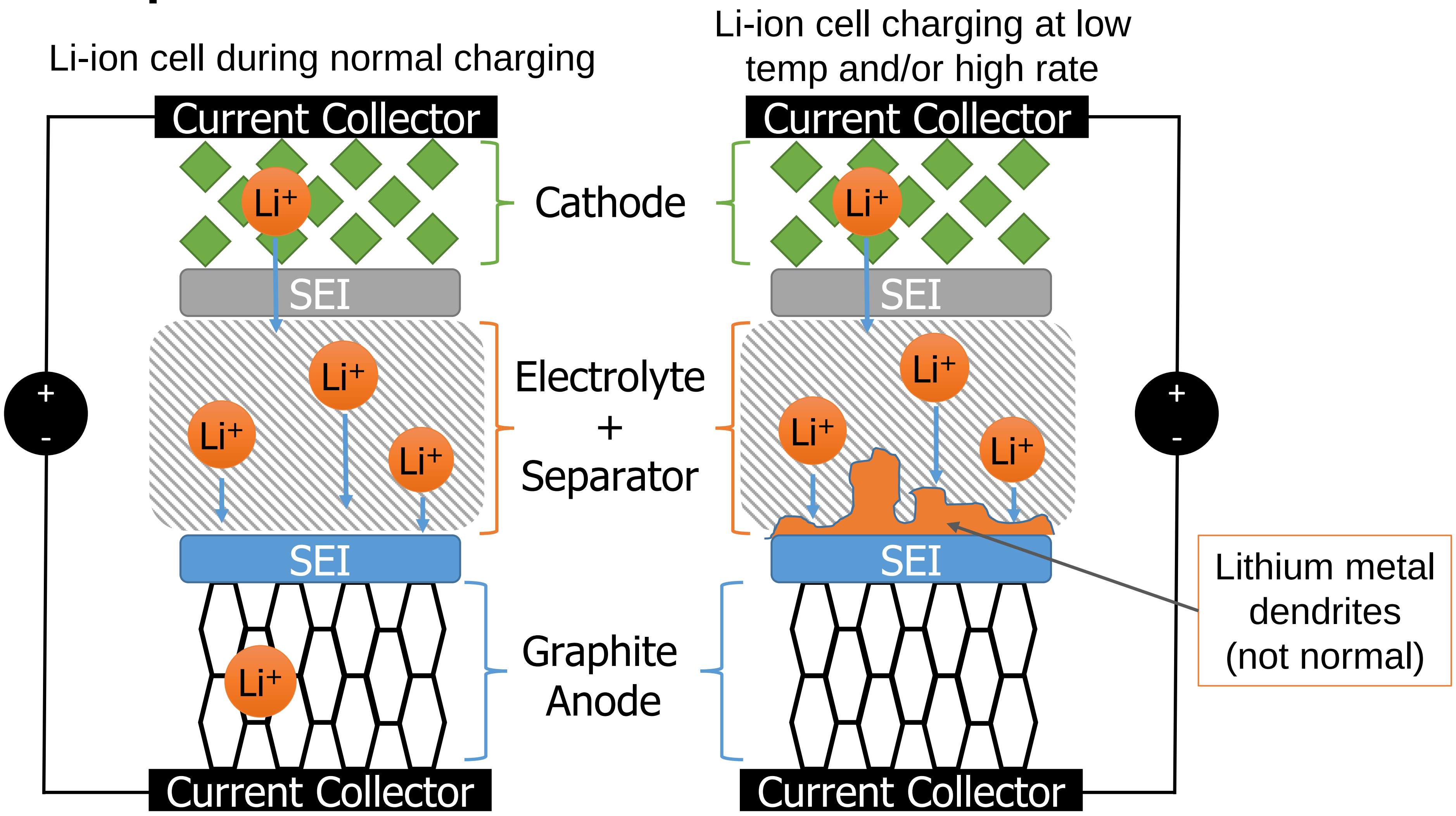


Lithium Primary Battery Conclusions

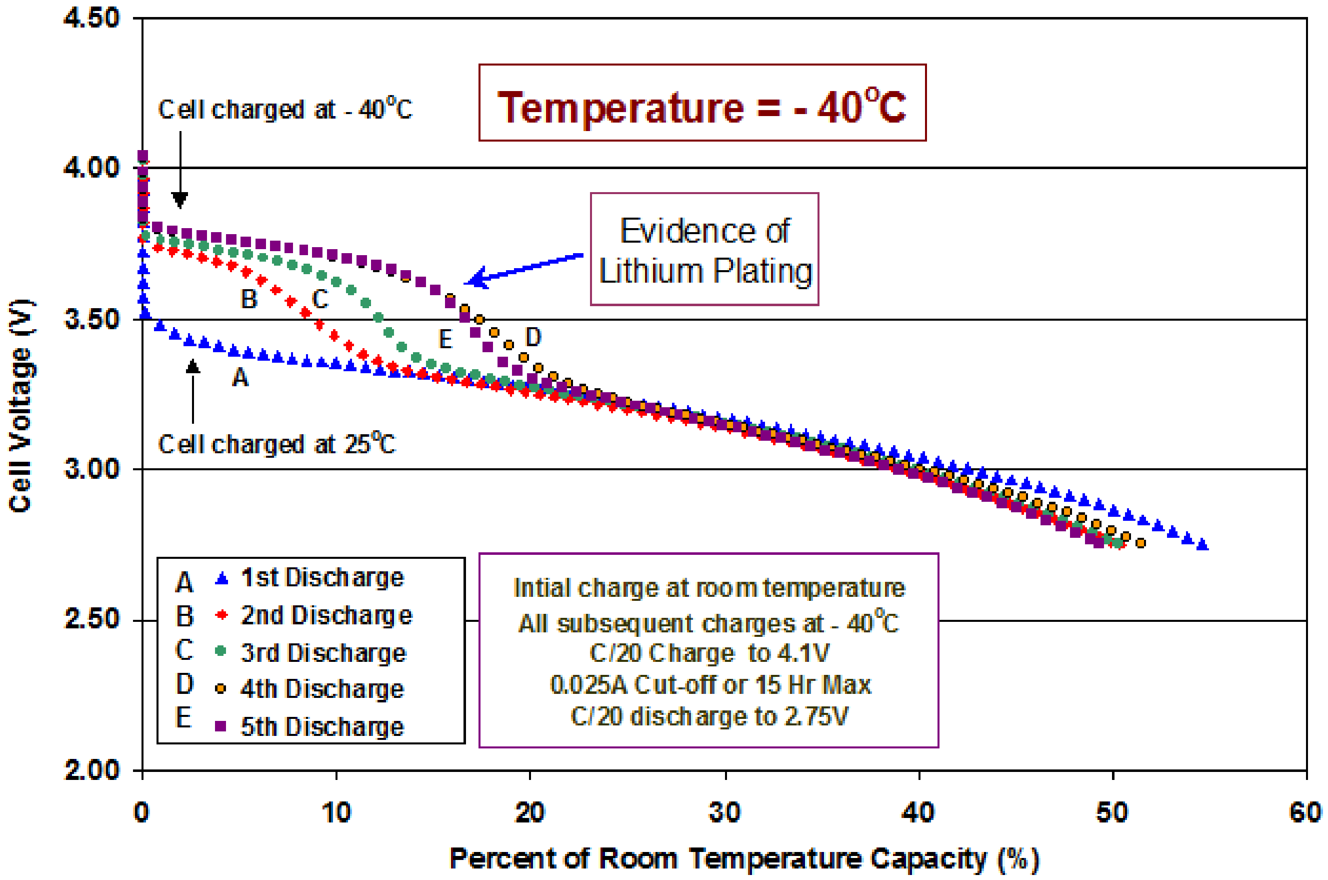
- High specific energy (730 Wh/kg) available from Li/CF_x cells
  - >2X more than heritage Li/$SOCl_2$ cells
  - Low temperature/high rate performance is poor
- Moderate specific energy (550 Wh/kg) available from improved Li/CF_x-MnO_2 cells
  - ~50 % higher than heritage Li/$SOCl_2$ cells
  - Still function at low temperature/high rate
- High dose radiation (up to 10 MRad) does not appear to significantly affect specific energy
  - Cell voltage is impacted
  - Impedance is not impacted
  - May be useful for planetary protection
- DHMR unlikely to be a viable option for Li/CF_x cells

Li/CF_x cell after heating to 170 °C

Secondary (Rechargeable) Batteries for Low Temperatures



Previous work at JPL to detect and quantify plating

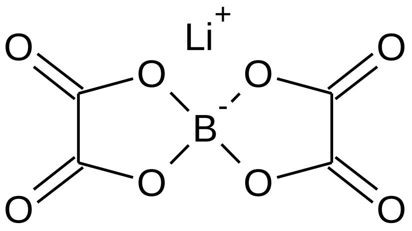


(1) M. C. Smart, B. V. Ratnakumar, L. Whitcanack, K. Chin, M. Rodriguez, and S. Surampudi, ***IEEE Aerospace and Electronic Systems Magazine***, 17 (12), 16-20 (2002).
(2) M. C. Smart and B. V. Ratnakumar, ***J. Electrochem. Soc***., ***158*** **(4)**, A379 (2011).

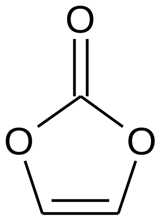
Impedance for Graphite/$LiNiCoAlO_2$ Cells at -30 °C

Baseline Electrolyte: 1.0 M $LiPF_6$ in EC+EMC+MP (20:20:60 vol. %)

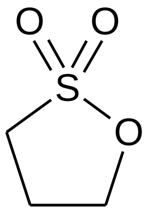
<u>Additives Investigated</u>



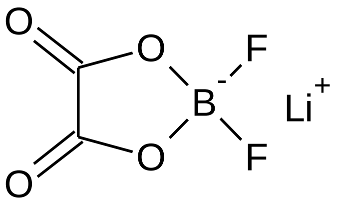
LiBOB



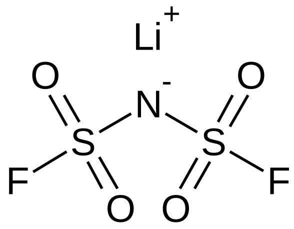
VC



PS

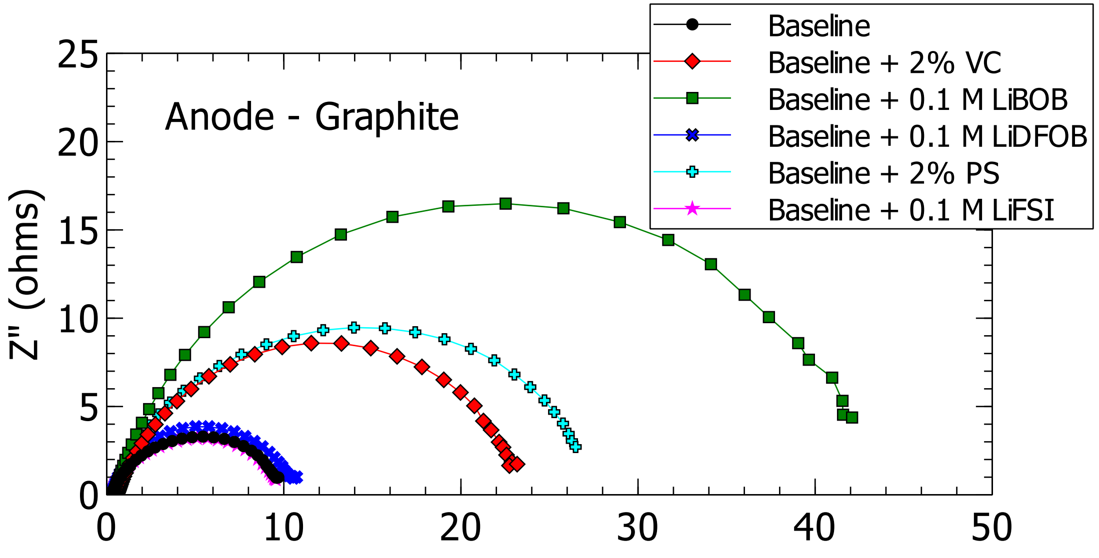


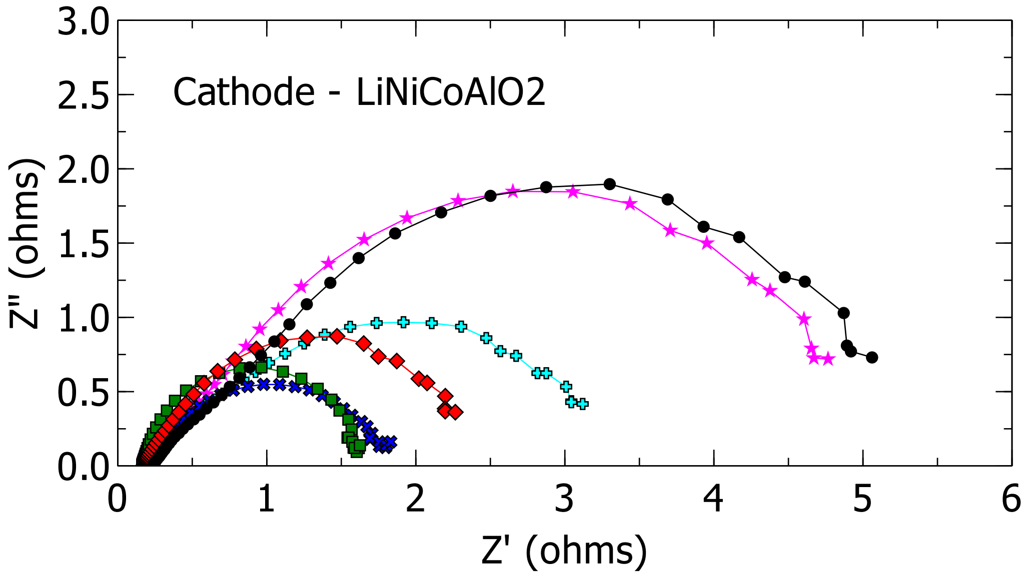
LiDFOB



LiFSI

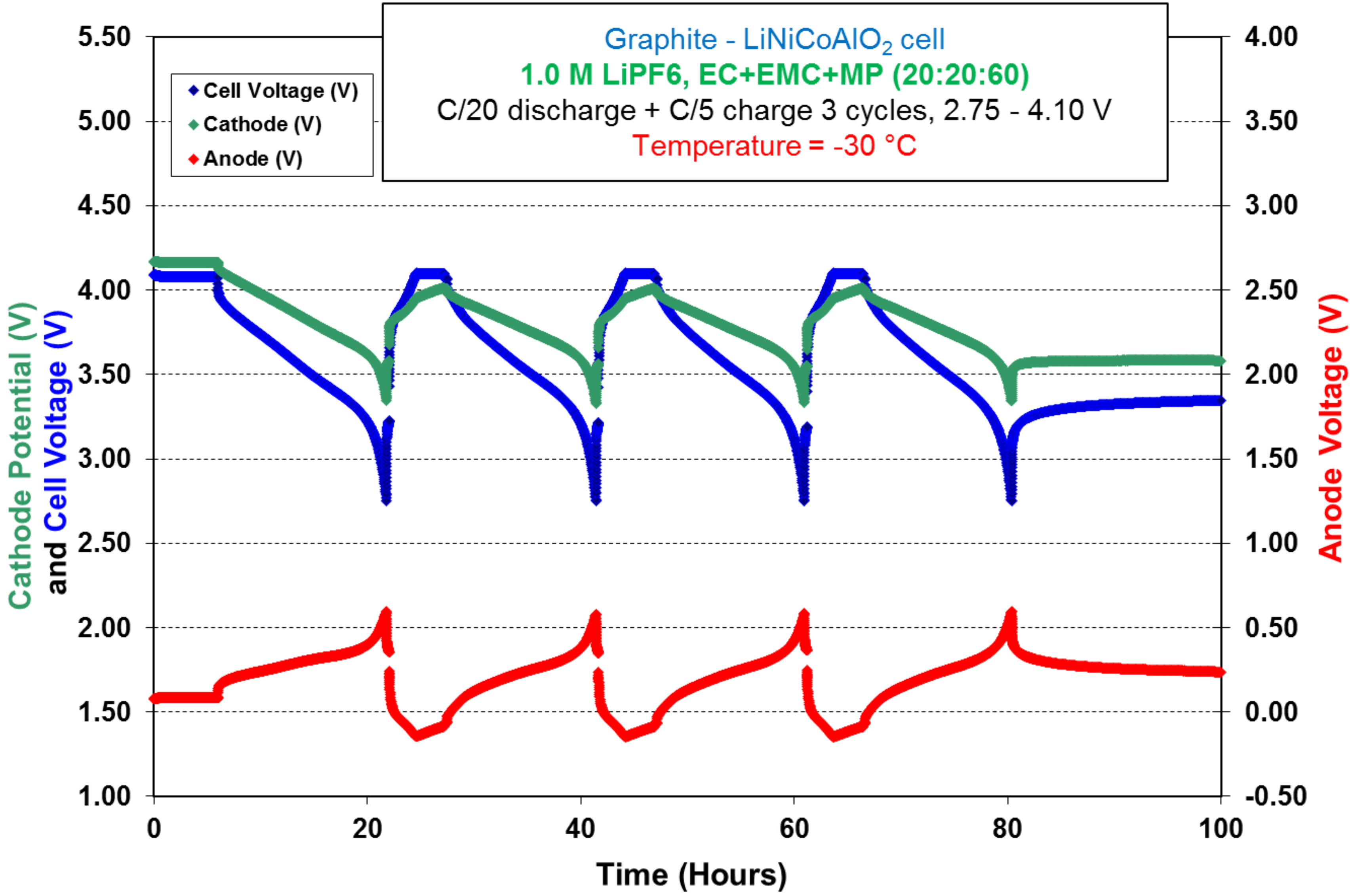
Anodes are more resistive than cathodes overall and additives other than LiFSI decrease cathode resistance and increase anode resistance





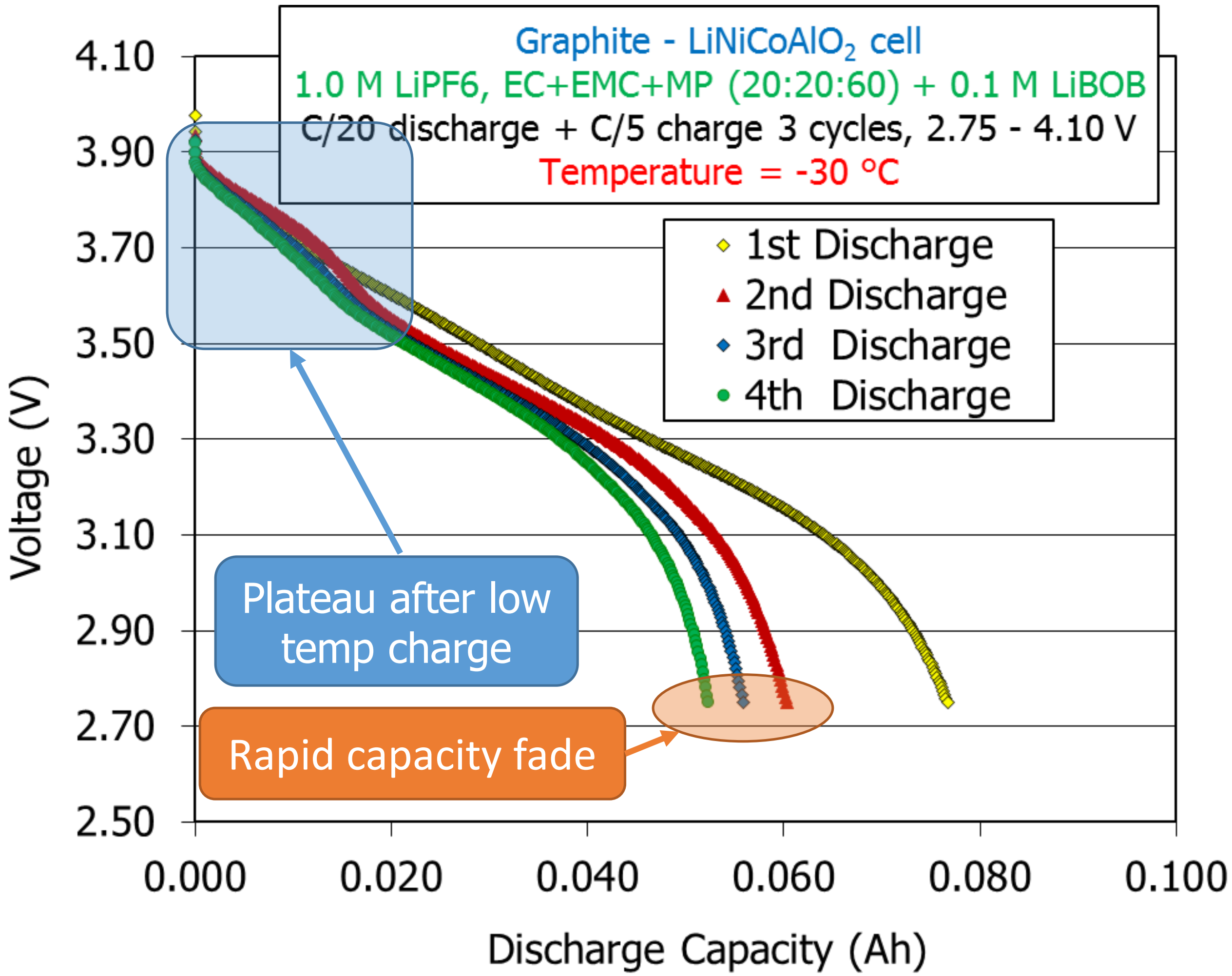
John-Paul Jones, Marshall C. Smart, Frederick C. Krause, Bugga V. Ratnakumar, and Erik J. Brandon. *Electrochemical Society Transactions*, **2017**, *75*, 1-11.

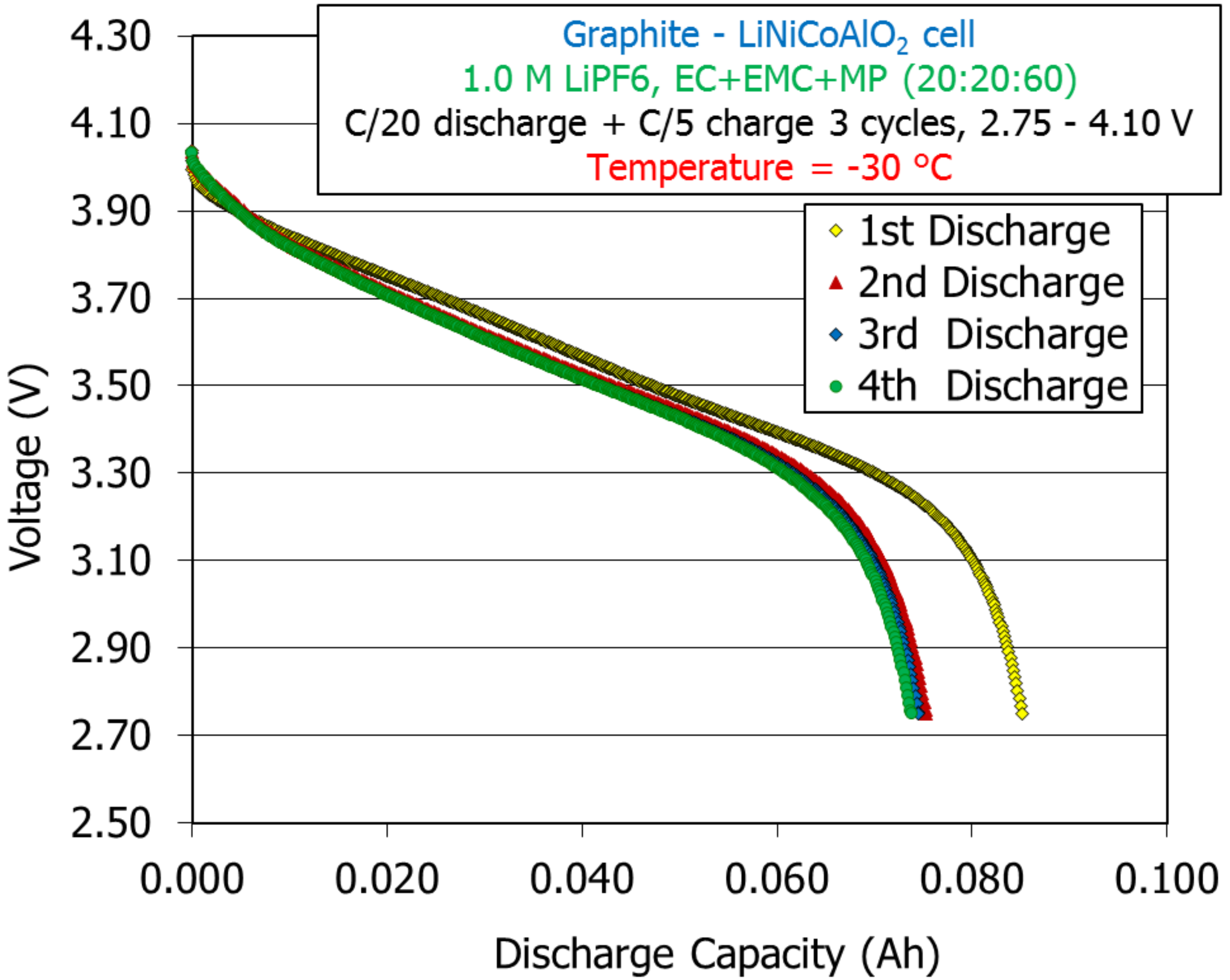
Testing Procedure to Detect Lithium Plating - Baseline



1. Charge at room temp
2. Discharge at C/20 at low temp
3. Charge at C/5 with C/50 taper at low temp
4. Discharge at C/20
5. Repeat steps 3 and 4 two more times

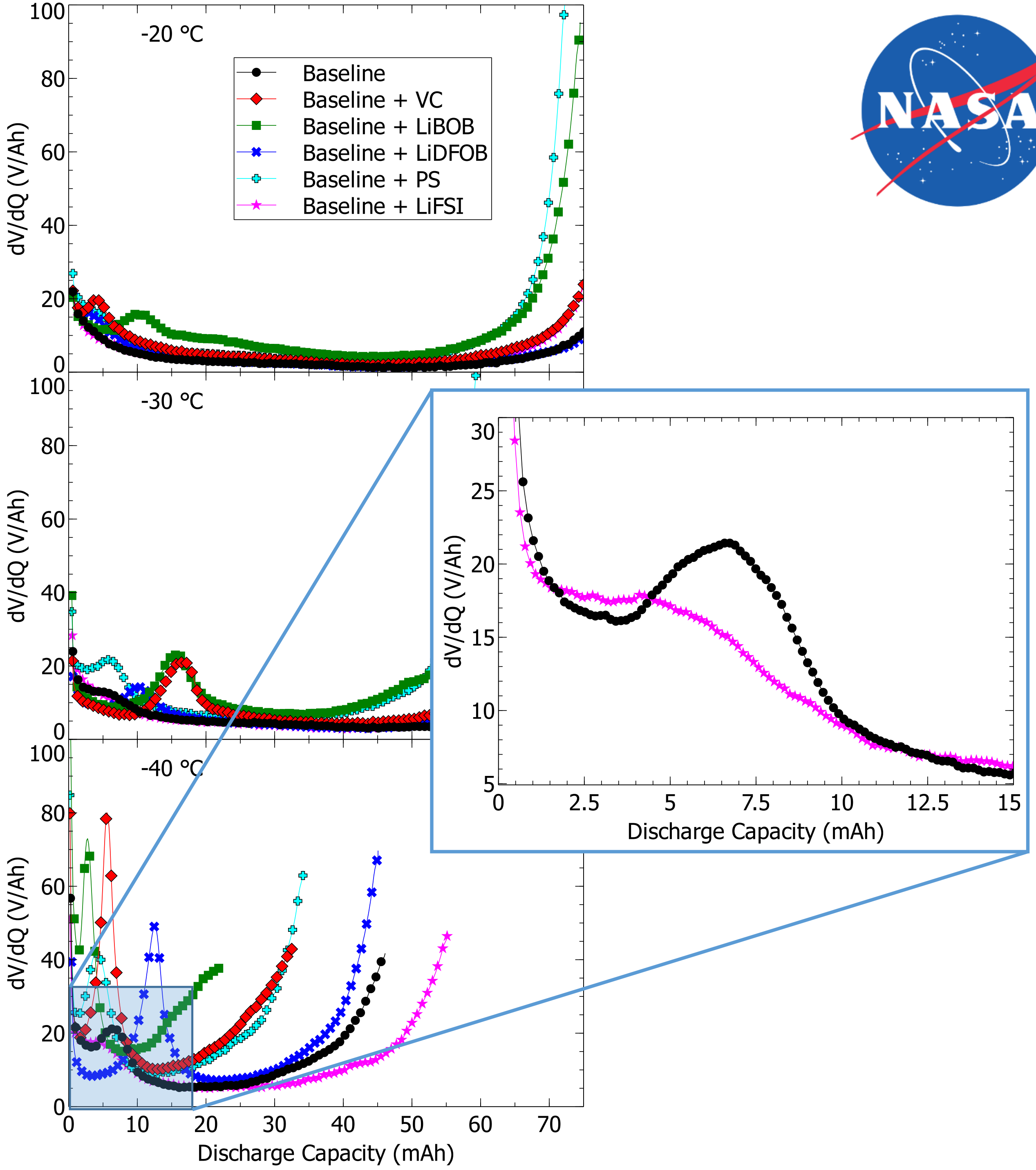
Testing Procedure to Detect Lithium Plating



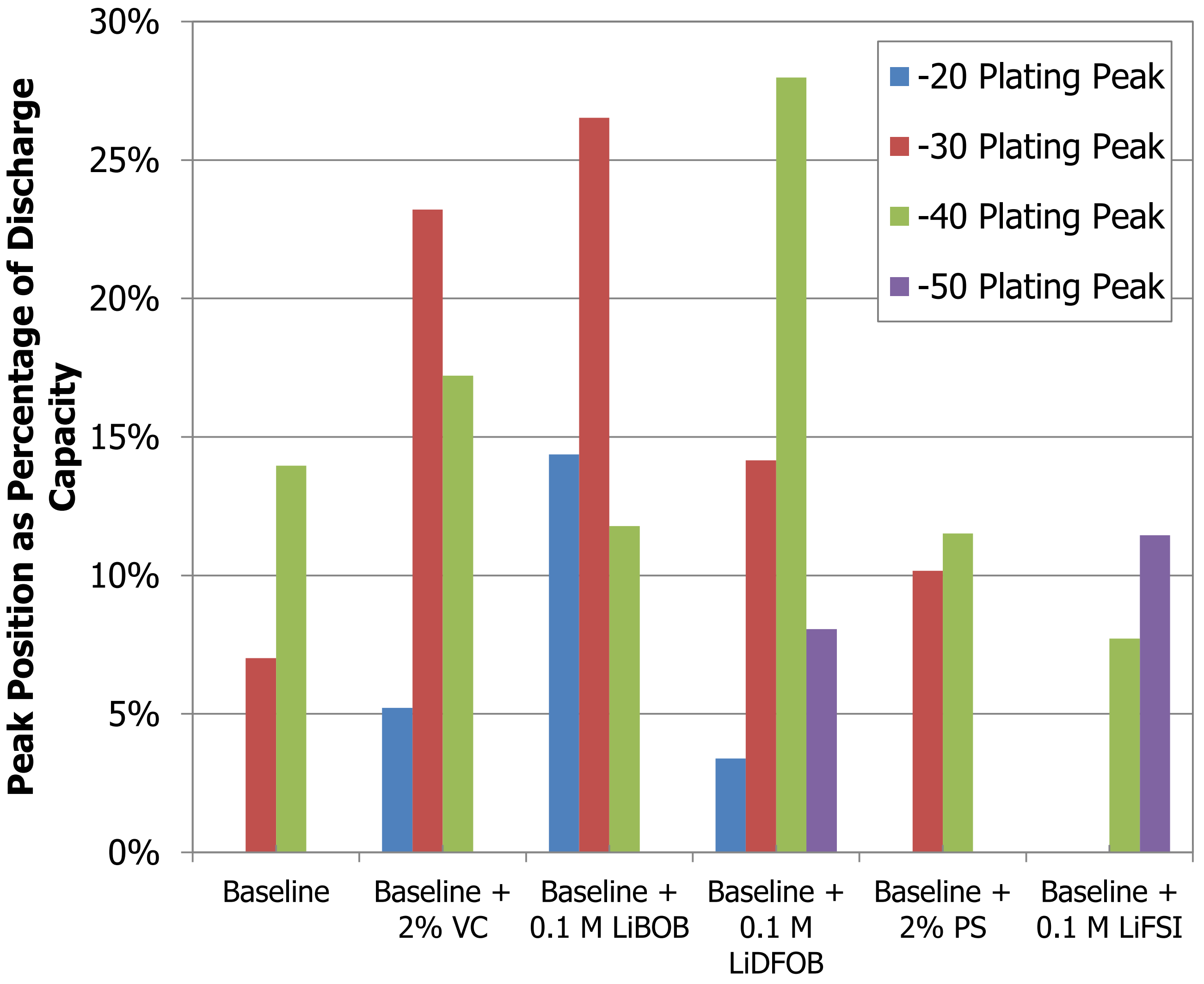


Comparison of Differential Capacity of Anodes at -20, -30, -40 °C

- No plating observed for baseline until -40 °C
- Cells with VC and LiBOB show evidence of plating at -20 °C and below
  - Lower temperature does not necessarily lead to increased plating
  - Cell with LiBOB produces substantially less plating at -40 °C than -30 °C
- Cells with PS and LiDFOB show plating at -30 °C
- Cell with LiFSI shows minimal evidence for plating even at -40 °C



Estimating Plating

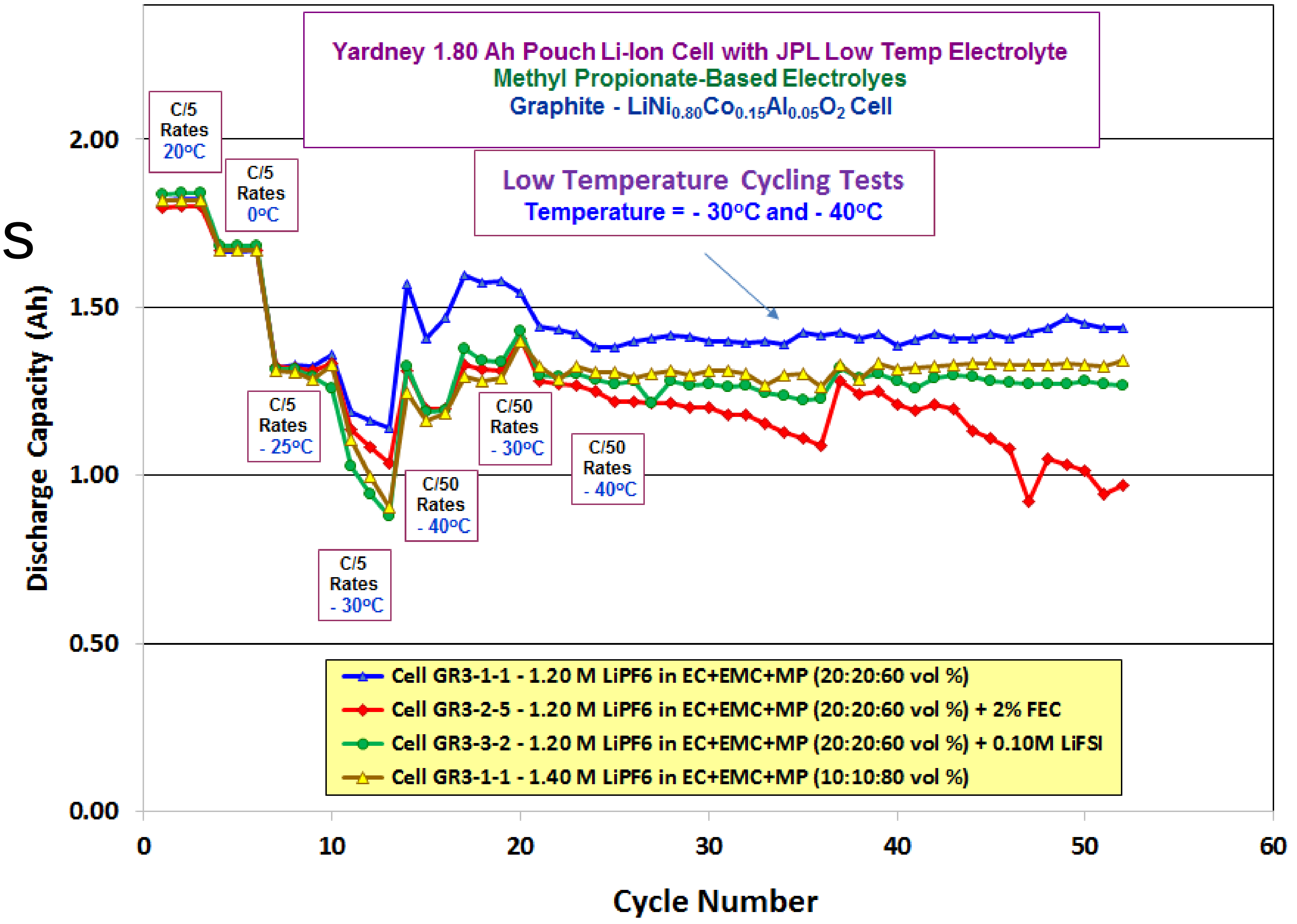


- ***Assume*** plated lithium is discharged first at low rates (C/20)*
  - Lithium stripping more facile than de-intercalation
- Peak position at maximum divided by total delivered capacity at that temperature
- Most electrolytes plate less lithium below a certain temperature
- LiFSI electrolyte displays significantly better performance than baseline during C/5 charging at low temperature
- -50 °C C/5 charging possible with only 11 % of capacity stored as plated lithium
- Despite good electrode kinetic data, LiDFOB does not perform better than baseline during plating
  - 28% lithium plating at -40 °C
- Other additives are all far worse than baseline

*Ref: M. Petzl and M. A. Danzer, *J. Power Sources*, ***254***, 80 (2014).

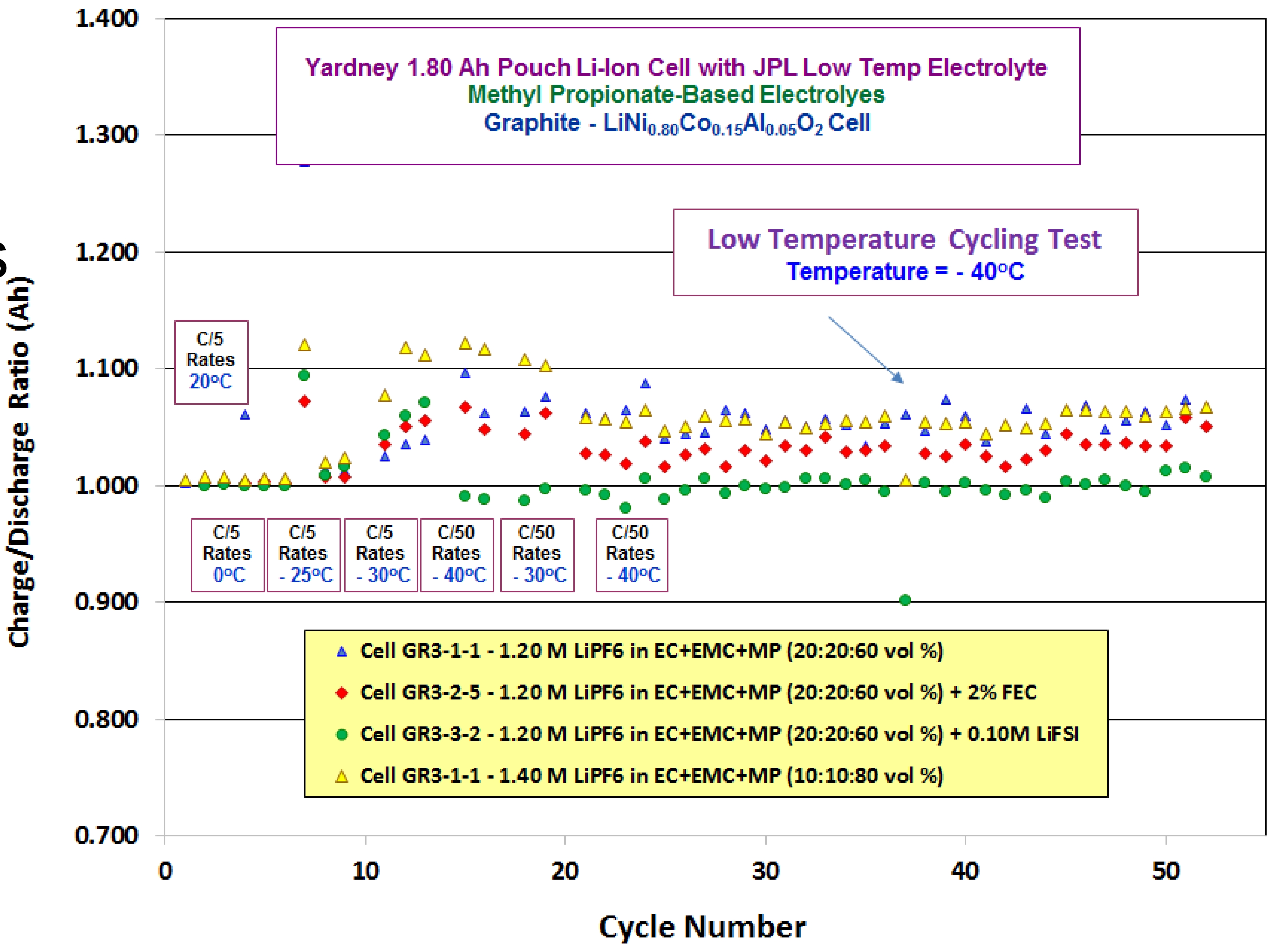
Evaluating New Electrolytes in Prototype Cells

Assessing the Charge Characteristics at Low Temperatures



Evaluating New Electrolytes in Prototype Cells

Assessing the Charge Characteristics at Low Temperatures



Conclusions

- Li/CF_x batteries can provide **>730 Wh/kg**
  - More than double Li/$SOCl_2$
  - Poor low temperature/high rate performance
- Improved Li/CF_x-MnO_2 hybrid batteries can provide **>550 Wh/kg**
  - Able to discharge at -40 °C
  - Compromise between capacity and low temperature/high rate
  - Appear to sustain gamma radiation without significant energy loss
- JPL-developed Li-ion electrolytes improve low temperature performance
  - Lithium plating can be an issue during charging
  - Improved lithium plating with 0.1 M LiFSI

Acknowledgements

People

- Marshall Smart
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Backup

Types of Batteries

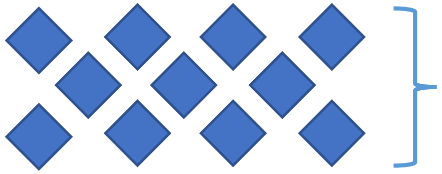
- Primary (single use)
  - ➢ Zn/MnO_2 (Alkaline)
  - ➢ Li/MnO_2
  - ➢ $Li/SOCl_2$
  - ➢ Li/SO_2
  - ➢ **Li/CF_x**
  - ➢ **Li/CF_x-MnO_2**

Not reversible

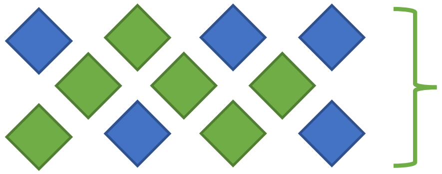
<u>Examples</u>

Li anode:
$Li \rightarrow Li^+ + e^-$

MnO_2 cathode:
$MnO_2 + Li^+ + e^- \rightarrow LiMnO_2$



CF_x Cathode



CF_x-MnO_2 Cathode

- Secondary (rechargeable)
  - ➢ Lead acid
  - ➢ Ni/H_2
  - ➢ Ni/Cd
  - ➢ Ni/MH (nickel metal hydride)
  - ➢ **Li-ion** (various)

Reversible

Carbon anode:
$LiC_6 \leftrightarrow C_6 + Li^+ + e^-$

$LiCoO_2$ cathode:
$Li_{1-x}CoO_2 + XLi^+ + e^- \leftrightarrow Li_xCoO_2$